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Optimized Synthesis, Structural Investigations, Ligand Tuning and Synthetic Evaluation of Silyloxy-Based Alkyne Metathesis Catalysts**

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Crystallographic Abstracts and Additional Structural Information

CCDC 846099 (42), 846100 (34a), 846102 (21a), 846103 (21b), 846104 (34c), 846106 (39), 846107 (8d), 846108 (38), 846109 (41), 867604 (43), 846110 (29), 846111 (26), 846112 (44), 846113 (31), 846114 (34b), 846115 (8c), 846116 (33), 846117 (28), 846118 (40), 846119 (35), 855527 (32) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

X-ray Crystal Structure Analysis of Complex 8d: $C_{75}H_{62}MoN_2O_3Si_3 \cdot CH_2Cl_2$, $M_r = 1304.40 \text{ g} \cdot \text{mol}^{-1}$, blue block, crystal size 0.35 x 0.29 x 0.10 mm, monoclinic, space group $P2_1/c$, $a = 13.9172(17) \text{ \AA}$, $b = 25.2768(10) \text{ \AA}$, $c = 19.336(3) \text{ \AA}$, $\beta = 109.425(9)^\circ$, $V = 6414.9(12) \text{ \AA}^3$, $T = 100 \text{ K}$, $Z = 4$, $D_{calc} = 1.351 \text{ g} \cdot \text{cm}^{-3}$, $\lambda = 0.71073 \text{ \AA}$, $\mu(Mo-K\alpha) = 0.395 \text{ mm}^{-1}$, Semi-empirical absorption correction ($T_{min} = 0.60$, $T_{max} = 0.75$), Bruker AXS Enraf-Nonius KappaCCD diffractometer, $2.66 < \theta < 27.50^\circ$, 73416 measured reflections, 14730 independent reflections, 12339 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.037 [I > 2\sigma(I)]$, $wR_2 = 0.087$, 783 parameters, H atoms riding. The crystal contains disordered dichloromethane (0.5:0.5). $S = 1.073$, residual electron density $+1.3 / -1.7 \text{ e} \text{ \AA}^{-3}$.

X-ray Crystal Structure Analysis of Complex 8c: $C_{74.25}H_{57.50}Cl_{0.50}F_3MoN_2O_3Si_3$, $M_r = 1280.66 \text{ g} \cdot \text{mol}^{-1}$, violet block, crystal size 0.36 x 0.32 x 0.07 mm, monoclinic, space group $P2_1/c$, $a = 20.497(3) \text{ \AA}$, $b = 19.469(3) \text{ \AA}$, $c = 16.890(3) \text{ \AA}$, $\beta = 97.473(2)^\circ$, $V = 6682.7(17) \text{ \AA}^3$, $T = 100 \text{ K}$, $Z = 4$, $D_{calc} = 1.273 \text{ g} \cdot \text{cm}^{-3}$, $\lambda = 0.71073 \text{ \AA}$, $\mu(Mo-K\alpha) = 0.326 \text{ mm}^{-1}$, Semi-empirical absorption correction ($T_{min} = 0.88$, $T_{max} = 0.97$), Bruker-AXS Kappa Mach3 APEX-II diffractometer, $1.45 < \theta < 31.63^\circ$, 200663 measured reflections, 22418 independent reflections, 17302 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.077 [I > 2\sigma(I)]$, $wR_2 = 0.219$, 732 parameters, H atoms riding. The structure contains a rotationally disordered trifluoromethane and positionally disordered phenyl and 1,10-phenanthroline groups (0.5:0.5). $S = 1.106$, residual electron density $+1.8 / -1.0 \text{ e} \text{ \AA}^{-3}$.

X-ray Crystal Structure Analysis of Complex 8d: $C_{75}H_{62}MoN_2O_3Si_3 \cdot CH_2Cl_2$, $M_r = 1304.40 \text{ g} \cdot \text{mol}^{-1}$, blue block, crystal size 0.35 x 0.29 x 0.10 mm, monoclinic, space group $P2_1/c$, $a = 13.9172(17) \text{ \AA}$, $b = 25.2768(10) \text{ \AA}$, $c = 19.336(3) \text{ \AA}$, $\beta = 109.425(9)^\circ$, $V = 6414.9(12) \text{ \AA}^3$, $T = 100 \text{ K}$, $Z = 4$, $D_{calc} = 1.351 \text{ g} \cdot \text{cm}^{-3}$, $\lambda = 0.71073 \text{ \AA}$, $\mu(Mo-K\alpha) = 0.395 \text{ mm}^{-1}$, Semi-empirical absorption correction ($T_{min} = 0.60$, $T_{max} = 0.75$), Bruker AXS Enraf-Nonius KappaCCD diffractometer, $2.66 < \theta < 27.50^\circ$, 73416 measured reflections, 14730 independent reflections, 12339 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.037 [I > 2\sigma(I)]$, $wR_2 = 0.087$, 783 parameters, H atoms riding. The crystal contains disordered dichloromethane (0.5:0.5). $S = 1.073$, residual electron density $+1.3 / -1.7 \text{ e} \text{ \AA}^{-3}$.

X-ray Crystal Structure Analysis of Complex 21a: $C_{64}H_{53}MoN_3O_3Si_3$, $M_r = 1092.30 \text{ g} \cdot \text{mol}^{-1}$, yellow block, crystal size 0.17 x 0.11 x 0.10 mm, orthorhombic, space group $Pna2_1$, $a = 13.918(3) \text{ \AA}$, $b = 9.7546(15) \text{ \AA}$, $c = 24.7204(9) \text{ \AA}$, $V = 5395.1(12) \text{ \AA}^3$, $T = 100 \text{ K}$, $Z = 4$, $D_{calc} = 1.345 \text{ g} \cdot \text{cm}^{-3}$, $\lambda = 0.71073 \text{ \AA}$,

$\mu(Mo-K_{\alpha}) = 0.360 \text{ mm}^{-1}$, Semi-empirical absorption correction ($T_{\min} = 0.95$, $T_{\max} = 0.98$), Bruker AXS Enraf-Nonius KappaCCD diffractometer, $2.77 < \theta < 30.16^{\circ}$, 36513 measured reflections, 15397 independent reflections, 12100 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.048 [I > 2\sigma(I)]$, $wR_2 = 0.094$, 668 parameters, absolute structure parameter = 0.00(11), H atoms riding, $S = 1.065$, residual electron density $+0.5 / -1.1 \text{ e } \text{\AA}^{-3}$.

X-ray Crystal Structure Analysis of Complex 21b: $2(C_{72}H_{69}MoN_3O_3Si_3) \cdot 2(C_7H_8)$, $M_r = 2678.38 \text{ g} \cdot \text{mol}^{-1}$, yellow block, crystal size $0.26 \times 0.25 \times 0.14 \text{ mm}$, monoclinic, space group $C2/c$, $a = 23.4027(15) \text{ \AA}$, $b = 13.7262(13) \text{ \AA}$, $c = 44.194(4) \text{ \AA}$, $\beta = 96.500(6)^{\circ}$, $V = 14105(2) \text{ \AA}^3$, $T = 100 \text{ K}$, $Z = 4$, $D_{\text{calc}} = 1.261 \text{ g} \cdot \text{cm}^3$, $\lambda = 0.71073 \text{ \AA}$, $\mu(Mo-K_{\alpha}) = 0.288 \text{ mm}^{-1}$, Semi-empirical absorption correction ($T_{\min} = 0.93$, $T_{\max} = 0.95$), Bruker AXS Enraf-Nonius KappaCCD diffractometer, $2.69 < \theta < 27.50^{\circ}$, 82431 measured reflections, 16001 independent reflections, 14829 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.097 [I > 2\sigma(I)]$, $wR_2 = 0.222$, 843 parameters, H atoms riding. The crystal contains solute toluene. $S = 1.382$, residual electron density $+1.8 / -2.0 \text{ e } \text{\AA}^{-3}$.

X-ray Crystal Structure Analysis of Complex 26: $C_{83}H_{75}KMoO_6Si_4 \cdot C_4H_{10}O$, $M_r = 1489.95 \text{ g} \cdot \text{mol}^{-1}$, red block, crystal size $0.164 \times 0.120 \times 0.076 \text{ mm}$, monoclinic, space group $P2_1/c$, $a = 13.412(4) \text{ \AA}$, $b = 16.649(5) \text{ \AA}$, $c = 34.798(10) \text{ \AA}$, $\beta = 94.917(6)^{\circ}$, $V = 7742(4) \text{ \AA}^3$, $T = 100 \text{ K}$, $Z = 4$, $D_{\text{calc}} = 1.278 \text{ g} \cdot \text{cm}^3$, $\lambda = 0.71073 \text{ \AA}$, $\mu(Mo-K_{\alpha}) = 0.340 \text{ mm}^{-1}$, Semi-empirical absorption correction ($T_{\min} = 0.95$, $T_{\max} = 0.98$), Bruker-AXS Kappa Mach3 APEX-II diffractometer, $1.36 < \theta < 27.50^{\circ}$, 177141 measured reflections, 17783 independent reflections, 13563 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.038 [I > 2\sigma(I)]$, $wR_2 = 0.106$, 905 parameters, H atoms riding. The crystal contains solute diethylether. $S = 1.077$, residual electron density $+1.1 / -0.9 \text{ e } \text{\AA}^{-3}$.

X-ray Crystal Structure Analysis of Complex 28: $C_{79}H_{65}KMoO_4Si_4$, $M_r = 1325.71 \text{ g} \cdot \text{mol}^{-1}$, violet block, crystal size $0.25 \times 0.22 \times 0.10 \text{ mm}$, monoclinic, space group $P2_1/c$, $a = 14.556(2) \text{ \AA}$, $b = 25.621(4) \text{ \AA}$, $c = 35.766(2) \text{ \AA}$, $\beta = 94.528(8)^{\circ}$, $V = 13296(3) \text{ \AA}^3$, $T = 200 \text{ K}$, $Z = 8$, $D_{\text{calc}} = 1.325 \text{ g} \cdot \text{cm}^3$, $\lambda = 0.71073 \text{ \AA}$, $\mu(Mo-K_{\alpha}) = 0.383 \text{ mm}^{-1}$, Semi-empirical absorption correction ($T_{\min} = 0.92$, $T_{\max} = 0.96$), Bruker AXS Enraf-Nonius KappaCCD diffractometer, $2.64 < \theta < 28.04^{\circ}$, 187409 measured reflections, 32135 independent reflections, 20663 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.053 [I > 2\sigma(I)]$, $wR_2 = 0.140$, 1603 parameters, H atoms riding. The crystal contains two independent molecules in the asymmetric unit, which differ in the conformations of the phenyl groups. $S = 1.090$, residual electron density $+0.9 / -1.5 \text{ e } \text{\AA}^{-3}$.

X-ray Crystal Structure Analysis of Complexes 29: $C_{61}H_{66}Mo_{1.04}O_4Si_4$, $M_r = 1291.94 \text{ g} \cdot \text{mol}^{-1}$, yellow block, crystal size $0.16 \times 0.11 \times 0.09 \text{ mm}$, triclinic, space group $P\bar{1}$, $a = 13.8399(13) \text{ \AA}$, $b = 21.659(3) \text{ \AA}$, $c = 22.470(3) \text{ \AA}$, $\alpha = 77.738(10)^{\circ}$, $\beta = 85.388(9)^{\circ}$, $\gamma = 89.992(7)^{\circ}$, $V = 6559.8(13) \text{ \AA}^3$, $T = 100 \text{ K}$, $Z = 4$, $D_{\text{calc}} = 1.308 \text{ g} \cdot \text{cm}^3$, $\lambda = 0.71073 \text{ \AA}$, $\mu(Mo-K_{\alpha}) = 0.333 \text{ mm}^{-1}$, Gaussian absorption correction ($T_{\min} = 0.352$, $T_{\max} = 0.858$), Bruker AXS Enraf-Nonius KappaCCD diffractometer, $2.61 < \theta < 33.13^{\circ}$, 202310

measured reflections, 49801 independent reflections, 34841 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.612$ [$I > 2\sigma(I)$], $wR_2 = 0.139$, 1634 parameters, H atoms riding. One of the phenyl groups is rotationally disordered over two positions. Refinement of the structure revealed the presence of a region of high residual electron density between Mo(2) and O8. Careful inspection of the structure, especially considering the approximate equality of the Mo(1)...O(4) and Mo(2)...O(8) distances, suggested that the electron density is an artefact. Indeed, the position of the phantom peak appeared to be related to that of Mo(1) by the translation vector (-0.5,0.0,0.5), indicating that the crystal contained a satellite or was in some way twinned. A twinning law was not obvious, though the fact that the gamma angle is $89.99(7)^\circ$ is somewhat suspicious. A pseudo atom Mo(1A) was included in the structural model and its occupancy and isotropic atomic displacement parameter refined. The occupancy refined to 0.084(1). Judging by the refined occupancy of Mo(1A), the extent of twinning can be estimated to be approximately 4% of the total weight, based on Mo. The sample contained crystals of varying quality and several crystals were looked at. The results described here represent those of the best crystal that was studied. Interestingly, the probable positions of the OH H atoms on both crystallographically independent triphenylsilanol molecules could be obtained from a difference Fourier synthesis and their positions and isotropic atomic displacement parameters refined successfully, albeit with somewhat short O-H distances, indicative of libration. $S = 1.349$, residual electron density $+3.78$ [0.60 Å from Mo(1A)]/ -2.52 [0.47 Å from Mo(2)] $e \text{ \AA}^{-3}$.

X-ray Crystal Structure Analysis of Complex 31: $C_{63}H_{54}MoO_3Si_3 \cdot CH_2Cl_2$, $M_r = 1124.20 \text{ g} \cdot \text{mol}^{-1}$, orange block, crystal size 0.17 x 0.14 x 0.07 mm, triclinic, space group $P\bar{1}$, $a = 10.9446(12) \text{ \AA}$, $b = 14.0009(16) \text{ \AA}$, $c = 20.028(2) \text{ \AA}$, $\alpha = 79.736(2)^\circ$, $\beta = 83.815(2)^\circ$, $\gamma = 67.340(2)^\circ$, $V = 2784.2(5) \text{ \AA}^3$, $T = 100 \text{ K}$, $Z = 2$, $D_{calc} = 1.341 \text{ g} \cdot \text{cm}^3$, $\lambda = 0.71073 \text{ \AA}$, $\mu(Mo-K_\alpha) = 0.442 \text{ mm}^{-1}$, Gaussian absorption correction ($T_{min} = 0.94$, $T_{max} = 0.98$), Bruker-AXS Kappa Mach3 APEX-II diffractometer, $1.03 < \theta < 31.16^\circ$, 82188 measured reflections, 17869 independent reflections, 15416 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.036$ [$I > 2\sigma(I)$], $wR_2 = 0.103$, 660 parameters, H atoms riding. The relatively anisotropic displacement parameters of C12-C14 indicated that one of the phenyl groups adopts slightly different conformations in the crystal. The disorder could, however, not be satisfactorily resolved owing to the two conformations being so similar. $S = 1.064$, residual electron density $+1.3$ [0.75 Å from Mo(1A)]/ $-1.4 e \text{ \AA}^{-3}$.

X-ray Crystal Structure Analysis of Complex 32: $C_{62}H_{52}MoSi_3O_4$, $M_r = 1041.25 \text{ g} \cdot \text{mol}^{-1}$, orange block, crystal size 0.18 x 0.18 x 0.14 mm, triclinic, space group $P\bar{1}$, $a = 11.1526(16) \text{ \AA}$, $b = 19.893(3) \text{ \AA}$, $c = 26.040(4) \text{ \AA}$, $\alpha = 112.164(2)^\circ$, $\beta = 99.707(3)^\circ$, $\gamma = 90.326(2)^\circ$, $V = 5258.5(13) \text{ \AA}^3$, $T = 100 \text{ K}$, $Z = 4$, $D_{calc} = 1.315 \text{ g} \cdot \text{cm}^3$, $\lambda = 0.71073 \text{ \AA}$, $\mu(Mo-K_\alpha) = 0.366 \text{ mm}^{-1}$, Semi-empirical absorption correction ($T_{min} = 0.92$, $T_{max} = 0.96$), Bruker-AXS Smart APEX-II diffractometer, diffractometer, $1.64 < \theta < 32.03^\circ$, 166048 measured reflections, 36620 independent reflections, 30545 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.033$ [$I > 2\sigma(I)$], $wR_2 = 0.088$, 643 parameters, H atoms riding. Several of the phenyl groups exhibit conformational

disorder (0.5:0.5). $S = 1.036$, residual electron density $+1.0 / -0.7 \text{ e } \text{\AA}^{-3}$.

X-ray Crystal Structure Analysis of Complex 33: $\text{C}_{75} \text{H}_{62} \text{Mo N}_2 \text{O}_3 \text{Si}_3$, $M_r = 1219.48 \text{ g} \cdot \text{mol}^{-1}$, violet block, crystal size $0.24 \times 0.15 \times 0.06 \text{ mm}$, monoclinic, space group $P2_1/c$, $a = 19.6238(17) \text{ \AA}$, $b = 19.6634(14) \text{ \AA}$, $c = 17.4740(18) \text{ \AA}$, $\beta = 106.360(8)^\circ$, $V = 6469.7(10) \text{ \AA}^3$, $T = 100 \text{ K}$, $Z = 4$, $D_{\text{calc}} = 1.252 \text{ g} \cdot \text{cm}^3$, $\lambda = 0.71073 \text{ \AA}$, $\mu(\text{Mo-K}\alpha) = 0.307 \text{ mm}^{-1}$, Semi-empirical absorption correction ($T_{\text{min}} = 0.94$, $T_{\text{max}} = 0.98$), Bruker AXS Enraf-Nonius KappaCCD diffractometer, $2.64 < \theta < 27.50^\circ$, 72745 measured reflections, 14850 independent reflections, 10990 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.056 [I > 2\sigma(I)]$, $wR_2 = 0.134$, 741 parameters, H atoms riding. Three of the phenyl groups are conformationally disordered (0.5:0.5). $S = 1.039$, residual electron density $+1.7 / -1.2 \text{ e } \text{\AA}^{-3}$.

X-ray Crystal Structure Analysis of Complex 34a: $\text{C}_{71} \text{H}_{58} \text{Mo N}_2 \text{O}_3 \text{Si}_3$, $M_r = 1167.40 \text{ g} \cdot \text{mol}^{-1}$, red block, crystal size $0.40 \times 0.34 \times 0.24 \text{ mm}$, monoclinic, space group $P2_1/c$, $a = 18.479(3) \text{ \AA}$, $b = 19.594(2) \text{ \AA}$, $c = 16.794(3) \text{ \AA}$, $\beta = 102.234(14)^\circ$, $V = 5942.5(16) \text{ \AA}^3$, $T = 200 \text{ K}$, $Z = 4$, $D_{\text{calc}} = 1.305 \text{ g} \cdot \text{cm}^3$, $\lambda = 0.71073 \text{ \AA}$, $\mu(\text{Mo-K}\alpha) = 0.331 \text{ mm}^{-1}$, Semi-empirical absorption correction ($T_{\text{min}} = 0.89$, $T_{\text{max}} = 0.94$), Bruker AXS Enraf-Nonius KappaCCD diffractometer, $2.69 < \theta < 35.08^\circ$, 164662 measured reflections, 26221 independent reflections, 14988 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.046 [I > 2\sigma(I)]$, $wR_2 = 0.116$, 721 parameters, H atoms riding, $S = 1.125$, residual electron density $+1.4 / -1.3 \text{ e } \text{\AA}^{-3}$.

X-ray Crystal Structure Analysis of Complex 34b: $\text{C}_{73} \text{H}_{62} \text{Mo N}_2 \text{O}_3 \text{Si}_3$, $M_r = 1195.46 \text{ g} \cdot \text{mol}^{-1}$, red block, crystal size $0.39 \times 0.36 \times 0.23 \text{ mm}$, monoclinic, space group $P2_1/c$, $a = 18.538(5) \text{ \AA}$, $b = 19.429(5) \text{ \AA}$, $c = 16.809(5) \text{ \AA}$, $\beta = 100.456(4)^\circ$, $V = 5954(3) \text{ \AA}^3$, $T = 100 \text{ K}$, $Z = 4$, $D_{\text{calc}} = 1.334 \text{ g} \cdot \text{cm}^3$, $\lambda = 0.71073 \text{ \AA}$, $\mu(\text{Mo-K}\alpha) = 0.332 \text{ mm}^{-1}$, Semi-empirical absorption correction ($T_{\text{min}} = 0.89$, $T_{\text{max}} = 0.92$), Bruker-AXS Kappa Mach3 APEX-II diffractometer, $1.62 < \theta < 36.68^\circ$, 228314 measured reflections, 29034 independent reflections, 24401 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.023 [I > 2\sigma(I)]$, $wR_2 = 0.080$, 741 parameters, H atoms riding, $S = 1.029$, residual electron density $+1.0 / -0.6 \text{ e } \text{\AA}^{-3}$.

X-ray Crystal Structure Analysis of Complex 34c: $\text{C}_{73} \text{H}_{61} \text{Mo N}_2 \text{O}_5 \text{Si}_3 \cdot \text{C}_4 \text{H}_{10} \text{O} \cdot 0.5 \text{C}_7 \text{H}_8$, $M_r = 1344.62 \text{ g} \cdot \text{mol}^{-1}$, violet block, crystal size $0.49 \times 0.33 \times 0.23 \text{ mm}$, monoclinic, space group $P2_1/c$, $a = 23.5105(8) \text{ \AA}$, $b = 19.0894(7) \text{ \AA}$, $c = 17.0118(6) \text{ \AA}$, $\beta = 105.260(2)^\circ$, $V = 7365.7(5) \text{ \AA}^3$, $T = 100 \text{ K}$, $Z = 4$, $D_{\text{calc}} = 1.213 \text{ g} \cdot \text{cm}^3$, $\lambda = 1.54184 \text{ \AA}$, $\mu(\text{Cu-K}\alpha) = 2.333 \text{ mm}^{-1}$, Semi-empirical absorption correction ($T_{\text{min}} = 0.37$, $T_{\text{max}} = 0.65$), Bruker AXS X8 Proteum diffractometer, $1.95 < \theta < 67.08^\circ$, 12908 measured reflections, 12908 independent reflections, 12030 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.044 [I > 2\sigma(I)]$, $wR_2 = 0.120$, 819 parameters, H atoms riding. The crystal contains solute dioxane and solute toluene and diether, which occupy the same region of space (0.5:0.5). One phenyl group is conformationally disordered (refined occupancy: 0.59(1):0.41(1)). $S = 1.048$, residual electron density $+2.0 / -0.7 \text{ e } \text{\AA}^{-3}$.

X-ray Crystal Structure Analysis of Complex 35: $\text{C}_{70} \text{H}_{58} \text{Cl}_2 \text{Mo N}_4 \text{O}_3 \text{Si}_3$, $M_r = 1254.31 \text{ g} \cdot \text{mol}^{-1}$, violet block, crystal size $0.30 \times 0.29 \times 0.10 \text{ mm}$, monoclinic, space group $P2_1/c$, $a = 13.7577(8) \text{ \AA}$, $b =$

15.8634(17) Å, $c = 28.390(3)$ Å, $\beta = 92.550(6)^\circ$, $V = 6189.9(9)$ Å³, $T = 100$ K, $Z = 4$, $D_{calc} = 1.346$ g · cm³, $\lambda = 0.71073$ Å, $\mu(Mo-K_\alpha) = 0.407$ mm⁻¹, Semi-empirical absorption correction ($T_{min} = 0.91$, $T_{max} = 0.97$), Bruker AXS Enraf-Nonius KappaCCD diffractometer, $2.67 < \theta < 34.99^\circ$, 147447 measured reflections, 27150 independent reflections, 20127 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.046$ [$I > 2\sigma(I)$], $wR_2 = 0.115$, 748 parameters, H atoms riding. The crystal contains solute dichloromethane. $S = 1.055$, residual electron density +1.1 / -1.9 e Å⁻³.

X-ray Crystal Structure Analysis of Complex 38: C₈₀ H₇₆ Mo N₂ O₁₂ Si₃ · 2(CH₂Cl₂), $M_r = 1607.49$ g · mol⁻¹, violet block, crystal size 0.30 x 0.24 x 0.24 mm, monoclinic, space group $P2_1/c$, $a = 47.123(2)$ Å, $b = 16.3237(8)$ Å, $c = 20.4173(9)$ Å, $\beta = 96.280(2)^\circ$, $V = 15611.3(12)$ Å³, $T = 100$ K, $Z = 8$, $D_{calc} = 1.368$ g · cm³, $\lambda = 1.54184$ Å, $\mu(Cu-K_\alpha) = 3.581$ mm⁻¹, Semi-empirical absorption correction ($T_{min} = 0.51$, $T_{max} = 0.67$), Bruker AXS X8 Proteum diffractometer, $1.89 < \theta < 67.42^\circ$, 352132 measured reflections, 27722 independent reflections, 26803 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.085$ [$I > 2\sigma(I)$], $wR_2 = 0.186$, 1884 parameters, H atoms riding. One of the methoxyphenyl groups in one of the two independent molecules in the asymmetric unit exhibits conformational disorder (0.5:0.5). $S = 1.242$, residual electron density +3.4 / -1.2 e Å⁻³.

X-ray Crystal Structure Analysis of Complex 39: C₃₇ H₆₃ Mo N₂ O_{3.50} Si₃, $M_r = 772.10$ g · mol⁻¹, orange block, crystal size 0.06 x 0.04 x 0.02 mm, monoclinic, space group $P2_1/n$, $a = 13.7325(17)$ Å, $b = 18.660(2)$ Å, $c = 17.569(2)$ Å, $\beta = 94.940(2)^\circ$, $V = 4485.3(9)$ Å³, $T = 100$ K, $Z = 4$, $D_{calc} = 1.143$ g · cm³, $\lambda = 0.71073$ Å, $\mu(Mo-K_\alpha) = 0.406$ mm⁻¹, Semi-empirical absorption correction ($T_{min} = 0.98$, $T_{max} = 0.99$), Bruker-AXS Kappa Mach3 APEX-II diffractometer, $1.81 < \theta < 27.50^\circ$, 102343 measured reflections, 10298 independent reflections, 9132 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.049$ [$I > 2\sigma(I)$], $wR_2 = 0.139$, 739 parameters, H atoms riding. One of the dimethyl-t-butyl-silyloxy group exhibits slight conformational disorder (0.85:0.15). $S = 1.199$, residual electron density +1.2 / -0.9 e Å⁻³.

X-ray Crystal Structure Analysis of Complex 40: C₁₀₆ H₈₉ Cl Mo₂ O₇ Si₅, $M_r = 1842.56$ g · mol⁻¹, green block, crystal size 0.36 x 0.16 x 0.08 mm, triclinic, space group $P\bar{1}$, $a = 15.2942(14)$ Å, $b = 16.0509(9)$ Å, $c = 22.525(3)$ Å, $\alpha = 100.687(9)^\circ$, $\beta = 90.009(9)^\circ$, $\gamma = 118.009(9)^\circ$, $V = 4773.0(8)$ Å³, $T = 100$ K, $Z = 2$, $D_{calc} = 1.282$ g · cm³, $\lambda = 0.71073$ Å, $\mu(Mo-K_\alpha) = 0.408$ mm⁻¹, Semi-empirical absorption correction ($T_{min} = 0.88$, $T_{max} = 0.97$), Bruker AXS Enraf-Nonius KappaCCD diffractometer, $2.66 < \theta < 32.58^\circ$, 138402 measured reflections, 34745 independent reflections, 23608 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.060$ [$I > 2\sigma(I)$], $wR_2 = 0.148$, 1092 parameters, H atoms riding, $S = 1.044$, residual electron density +1.1 / -2.4 e Å⁻³.

X-ray Crystal Structure Analysis of Complex 41: C₁₂₀ H₁₁₈ Cl₄ K₂ Mo₂ O₈ Si₆, $M_r = 2268.56$ g · mol⁻¹, red plate, crystal size 0.16 x 0.05 x 0.01 mm, triclinic, space group $P\bar{1}$, $a = 13.667(3)$ Å, $b = 14.741(4)$ Å, $c = 16.249(4)$ Å, $\alpha = 73.746(4)^\circ$, $\beta = 67.738(4)^\circ$, $\gamma = 67.110(4)^\circ$, $V = 2757.0(11)$ Å³, $T = 100$ K, $Z = 1$, $D_{calc} = 1.366$ g · cm³, $\lambda = 0.71073$ Å, $\mu(Mo-K_\alpha) = 0.522$ mm⁻¹, Semi-empirical absorption correction ($T_{min} =$

0.95, $T_{\max} = 1.00$), Bruker-AXS Kappa Mach3 APEX-II diffractometer, $1.37 < \theta < 34.02^\circ$, 93784 measured reflections, 22279 independent reflections, 14304 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.053 [I > 2\sigma(I)]$, $wR_2 = 0.150$, 643 parameters, H atoms riding. The crystal contains solute dichloromethane and disordered pentane (0.5:0.5). $S = 1.037$, residual electron density $+2.0 / -1.8 \text{ e } \text{\AA}^{-3}$.

X-ray Crystal Structure Analysis of Complex 42: $\text{C}_{46} \text{H}_{38} \text{Mo N}_2 \text{O}_4 \text{Si}_2$, $M_r = 834.90 \text{ g} \cdot \text{mol}^{-1}$, colourless block, crystal size $0.08 \times 0.06 \times 0.05 \text{ mm}$, orthorhombic, space group $Pbca$, $a = 13.1352(15) \text{ \AA}$, $b = 17.451(2) \text{ \AA}$, $c = 32.920(4) \text{ \AA}$, $V = 7546.0(15) \text{ \AA}^3$, $T = 100 \text{ K}$, $Z = 8$, $D_{\text{calc}} = 1.470 \text{ g} \cdot \text{cm}^3$, $\lambda = 0.71073 \text{ \AA}$, $\mu(\text{Mo-K}\alpha) = 0.460 \text{ mm}^{-1}$, Semi-empirical absorption correction ($T_{\min} = 0.97$, $T_{\max} = 0.98$), Bruker-AXS Smart APEX-II diffractometer, $4.08 < \theta < 33.21^\circ$, 204176 measured reflections, 14402 independent reflections, 12018 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.036 [I > 2\sigma(I)]$, $wR_2 = 0.101$, 496 parameters, H atoms riding, $S = 1.154$, residual electron density $+2.1 / -1.3 \text{ e } \text{\AA}^{-3}$.

X-ray Crystal Structure Analysis of Complex 43: $\text{C}_{133} \text{H}_{110} \text{Cl}_6 \text{Mo}_2 \text{N}_4 \text{O}_8 \text{Si}_4$, $M_r = 2409.20 \text{ g} \cdot \text{mol}^{-1}$, green block, crystal size $0.300 \times 0.105 \times 0.072 \text{ mm}$, triclinic, space group $P\bar{1}$, $a = 13.6231(18) \text{ \AA}$, $b = 13.8455(15) \text{ \AA}$, $c = 16.9715(13) \text{ \AA}$, $\alpha = 82.231(8)^\circ$, $\beta = 80.460(9)^\circ$, $\gamma = 70.091(11)^\circ$, $V = 2957.5(6) \text{ \AA}^3$, $T = 100 \text{ K}$, $Z = 1$, $D_{\text{calc}} = 1.353 \text{ g} \cdot \text{cm}^3$, $\lambda = 0.71073 \text{ \AA}$, $\mu(\text{Mo-K}\alpha) = 0.448 \text{ mm}^{-1}$, Semi-empirical absorption correction ($T_{\min} = 0.71$, $T_{\max} = 1.00$), Bruker AXS Enraf-Nonius KappaCCD diffractometer, $2.74 < \theta < 27.50^\circ$, 42554 measured reflections, 10476 independent reflections, 13542 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.074 [I > 2\sigma(I)]$, $wR_2 = 0.098$, 1092 parameters, H atoms riding. The crystal contains disordered dichloromethane. There was a significant fall-off in diffraction intensity with increasing resolution, probably due to loss of solvent from the crystal, resulting in a large suggested second parameter for the weighting scheme. Several reflections at low diffraction angles were affected by the beamstop and removed for the final refinement cycles. $S = 1.044$, residual electron density $+1.1 / -2.4 \text{ e } \text{\AA}^{-3}$.

X-ray Crystal Structure Analysis of 44: Tiny amounts ($< 5\%$) of crystals of another complex (**44**) formed by hydrolysis of $[(\text{Ph}_3\text{SiO})_4\text{Mo}\equiv\text{CPh}][\text{K}]$ were collected, in which oxo-bridged dimeric units are further aggregated by K^+ -counterions. As the crystal data were of insufficient quality and had to be treated with the SQUEEZE program, we refrain from a further discussion. $\text{C}_{36} \text{H}_{30} \text{K Mo O}_4 \text{Si}_2$, $M_r = 717.82 \text{ g} \cdot \text{mol}^{-1}$, orange block, crystal size $0.26 \times 0.16 \times 0.14 \text{ mm}$, triclinic, space group $P\bar{1}$, $a = 13.0912(16) \text{ \AA}$, $b = 16.7534(10) \text{ \AA}$, $c = 17.7456(16) \text{ \AA}$, $\alpha = 98.903(5)^\circ$, $\beta = 104.574(10)^\circ$, $\gamma = 106.073(8)^\circ$, $V = 3512.5(6) \text{ \AA}^3$, $T = 293(2) \text{ K}$, $Z = 4$, $D_{\text{calc}} = 1.357 \text{ g} \cdot \text{cm}^3$, $\lambda = 0.71073 \text{ \AA}$, $\mu(\text{Mo-K}\alpha) = 0.596 \text{ mm}^{-1}$, Semi-empirical absorption correction ($T_{\min} = 0.88$, $T_{\max} = 0.94$), Bruker AXS Enraf-Nonius KappaCCD diffractometer, $2.60 < \theta < 36.02^\circ$, 132181 measured reflections, 33270 independent reflections, 26385 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.037 [I > 2\sigma(I)]$, $wR_2 = 0.094$, 788 parameters, H atoms riding, $S = 1.048$, residual electron density $+1.6 / -1.1 \text{ e } \text{\AA}^{-3}$.

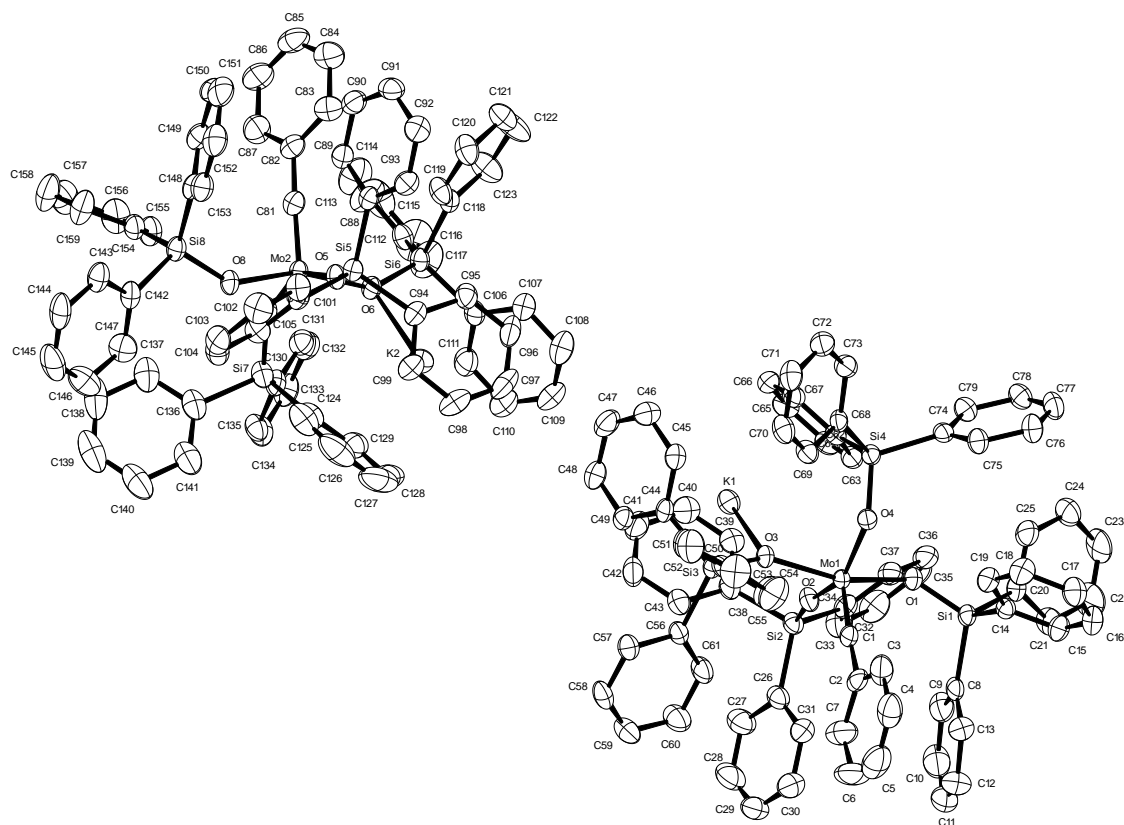


Figure S3. The two independent molecules of complex **28a** in the unit cell.

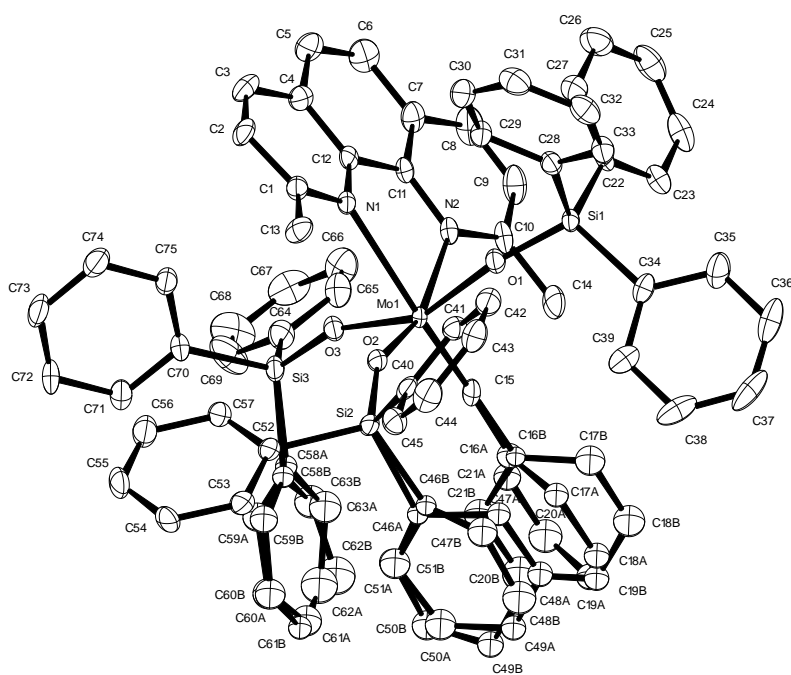


Figure S4. Structure of complex **33** in the solid state.

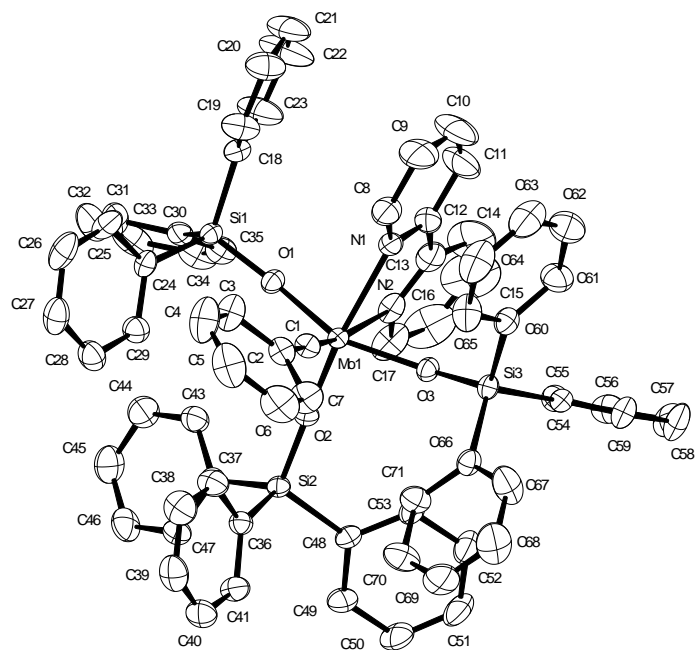


Figure S5. Structure of complex **34a** in the solid state.

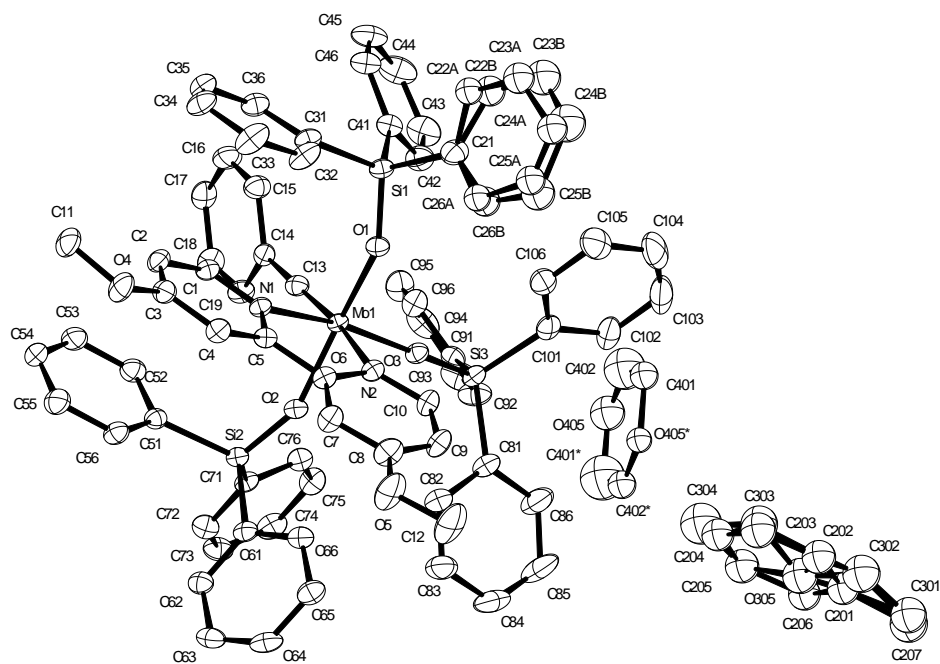


Figure S6. Structure of complex **34c** in the solid state.

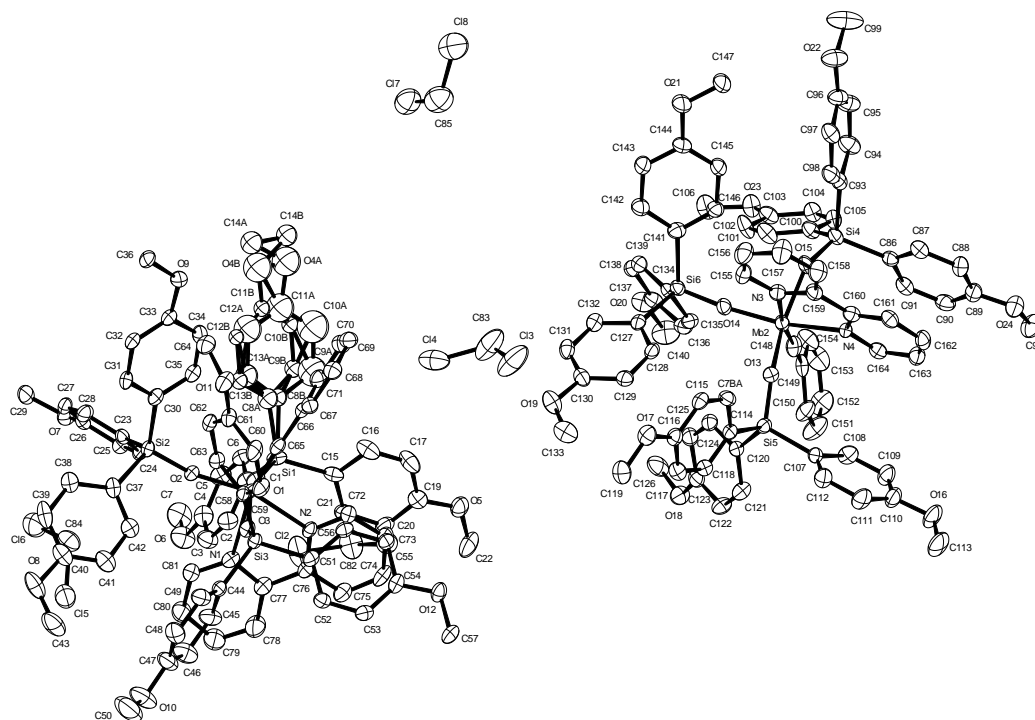


Figure S7. The two independent molecules of complex **38** in the unit cell.

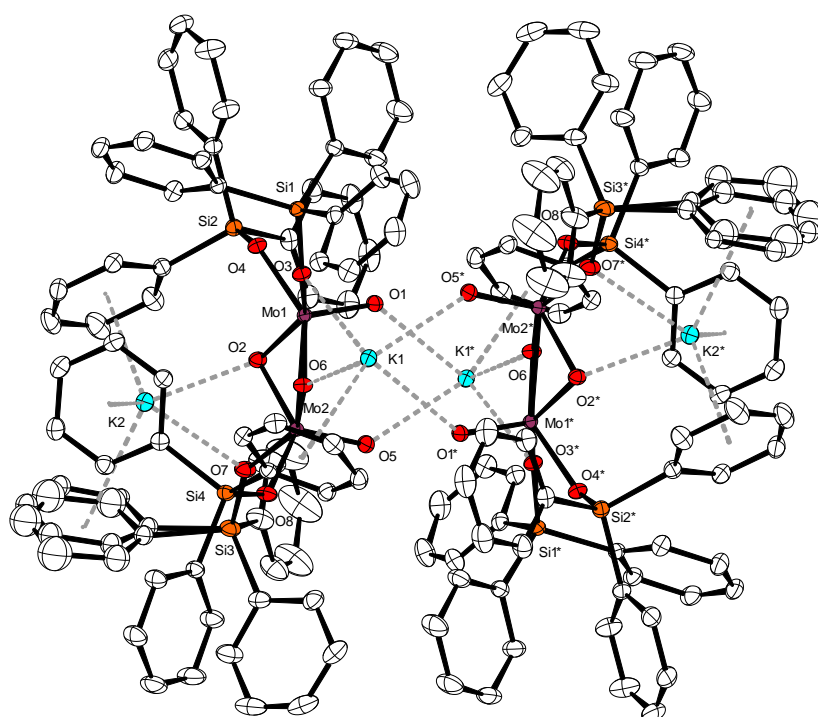


Figure S8. Additional decomposition product **44** obtained in low yield (< 5%) upon recrystallization of complex **27** from moist solvents; the crystal data were of insufficient quality and had to be treated with the SQUEEZE program, but the connectivity is convincing.

General. Unless stated otherwise, all reactions were carried out under Ar in flame-dried glassware. The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar: THF, Et₂O, 1,4-dioxane (Mg/anthracene), CH₂Cl₂, DME, MeCN (CaH₂), hexane, toluene (Na/K), MeOH (Mg). Flash chromatography (FC): Merck silica gel 60 (230–400 mesh). NMR: Spectra were recorded on Bruker DPX 300, AMX 300, AV 400, and AVIII 600 spectrometer in the solvents indicated; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale (CDCl₃: $\delta_C \equiv 77.0$ ppm; residual CHCl₃ in CDCl₃: $\delta_H \equiv 7.26$ ppm; CD₂Cl₂: $\delta_C \equiv 53.8$ ppm; residual ¹H: $\delta_H \equiv 5.32$ ppm; [D₈]-toluene: $\delta_C \equiv 20.7$ ppm; residual D₅C₆CD₂H: $\delta_H \equiv 2.09$ ppm). IR: Spectrum One (Perkin-Elmer) spectrometer, wavenumbers ($\tilde{\nu}$) in cm⁻¹. MS (EI): Finnigan MAT 8200 (70 eV), ESI-MS: ESQ3000 (Bruker), accurate mass determinations: Bruker APEX III FT-MS (7 T magnet) or Mat 95 (Finnigan). Melting points: Büchi melting point apparatus B-540 (corrected). Elemental analyses: H. Kolbe, Mülheim/Ruhr. Unless stated otherwise, all commercially available compounds (Fluka, Lancaster, Aldrich) were used as received.

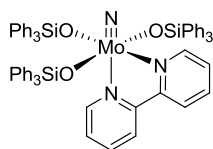
1,10-Phenanthroline and bipyridine were purified and dried by two subsequent sublimations of the commercial sample (Aldrich, $\geq 99\%$) under vacuum (10⁻³ mbar).

The molecular sieves used in this investigation were dried for 24 h at 280°C (sand bath) under vacuum prior to use and were stored and transferred under Ar.

Abbreviations: bipy = 2,2'-bipyridine; phen = 1,10-phenanthroline; dme = 1,2-dimethoxyethane

Nitrido Series: The preparation and characterization of complexes **2**, **3**, **19** is described in our previous publications.^{1,2}

[Mo(≡N)(OSiPh₃)₃](bipy) (21a). Ph₃SiOH (320 mg, 1.16 mmol) was added to a solution of [Mo(≡N)(OTMS)₂(N(TMS)₂)] (**19**) (173 mg, 0.39 mmol) in toluene (5 mL) under Argon. The resulting mixture was stirred for 1 h before 2,2'-



bipyridine (61 mg, 0.39 mmol) was added. After 1 h, the solvent was evaporated and the residue dried in vacuo (10⁻³ mbar) for 1 h at ambient temperature and then at 60°C. The remaining crude product was recrystallized from hot (105°C) toluene (2 mL) to give [Mo(≡N)(OSiPh₃)₃](bipy) (**21a**) as a yellow crystalline solid (336 mg, 79%). ¹H NMR (400 MHz, CD₂Cl₂): δ = 8.93 (dd, J = 5.5, 1.1 Hz, 1H), 8.72–8.71 (m, 1H), 7.81 (dd, J = 8.0, 1.6 Hz, 6H), 7.77 (td, J = 7.9, 1.6 Hz, 1H), 7.48 (d, J = 8.2 Hz, 1H), 7.39 (td, J = 7.9, 1.6 Hz, 1H), 7.27–7.16 (m, 23H), 7.07 (t, J = 7.8 Hz, 6H), 6.97 (t, J = 7.8 Hz, 12H), 6.73–6.70 (m, 1H); ¹³C NMR (100 MHz, CD₂Cl₂): δ = 156.5, 150.1, 149.9, 147.8, 139.5, 138.3, 138.0, 137.9, 136.1, 135.5, 135.3, 135.2, 129.6, 129.5, 128.8, 127.9, 127.8, 127.6, 125.6, 125.4, 122.1, 122.0.

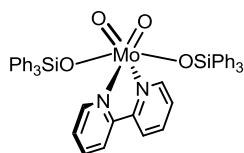
[Mo(≡N)(OSiPh₃)₃](4,4'-di-*tert*-butyl-2,2'-bipyridyl) (21b). Prepared analogously as a pale yellow solid. ¹H NMR (400 MHz, CD₂Cl₂): δ = 8.77 (d, J = 5.8 Hz, 1H), 8.59 (dd, J = 5.4, 0.4 Hz, 1H), 7.79–7.75 (m, 6H), 7.65–7.61 (m, 1H), 7.52–7.37 (m, 2H), 7.32–7.11 (m, 21H), 7.06–7.01 (m, 6H), 6.95 (t, J = 7.7 Hz, 12H), 6.68 (dd, J = 5.9, 2.0 Hz, 1H), 1.37 (s, 9H), 1.24 (s, 9H); ¹³C NMR (100 MHz, CD₂Cl₂): δ = 162.7, 162.5, 161.5, 155.2, 149.9, 149.4, 149.0, 148.9, 146.5,

1 J. Heppekausen, R. Stade, R. Goddard, A. Fürstner, *J. Am. Chem. Soc.* **2010**, *132*, 11045–11057.

2 M. Bindl, R. Stade, E. K. Heilmann, A. Picot, R. Goddard, A. Fürstner, *J. Am. Chem. Soc.* **2009**, *131*, 9468–9470.

137.0, 136.9, 136.7, 134.9, 134.4, 134.1, 134.0, 129.3, 128.3, 128.2, 127.9, 127.4, 127.2, 126.7, 126.6, 126.3, 34.4, 34.3, 34.2, 29.5, 29.4, 29.3; IR (ATR): 3063, 3044, 2973, 1957, 1887, 1822, 1615, 1587, 1551, 1494, 1483, 1461, 1427, 1407, 1363, 1304, 1249, 1186, 1152, 1111, 1026, 1009, 999, 935, 888, 850, 840, 739, 696 cm^{-1} ; MS (ESI⁻): m/z (%): 1206 (100) [M+H]; HRMS (ESI⁺): m/z : calcd for $\text{C}_{72}\text{H}_{69}\text{MoN}_3\text{O}_3\text{Si}_3+\text{H}$: 1206.3803; found: 1206.3782.

Hydrolysis Product 42: Ph_3SiOH (358 mg, 1.30 mmol) was added to a solution of $[\text{Mo}(\equiv\text{N})(\text{OTMS})_2(\text{N}(\text{TMS})_2)]$ (**19**) (194 mg, 432 μmol) in toluene (6.3 mL) and the resulting mixture stirred for 30 min at 80°C. After reaching ambient temperature, 2,2'-bipyridine (as purchased; un-sublimed, 67.4 mg, 432 μmol) was introduced and the mixture stirred for 18 h. Evaporation of all volatile materials followed by recrystallization of the



crude product from hot (80 °C) toluene gave complex **42** as a colorless solid. ^1H NMR (400 MHz, CD_2Cl_2): δ = 9.07-9.03 (m, 2H), 7.72 (td, J = 7.8, 1.6 Hz, 2H), 7.65-7.61 (m, 1H), 7.48-7.37 (m, 3H), 7.29-7.10 (m, 30H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 150.8, 139.4, 137.6, 135.2, 129.4, 128.3, 127.8, 126.0, 121.9; IR (ATR): 3068, 3050, 3002, 1891, 1822, 1666, 1602, 1594, 1572, 1485, 1474, 1439, 1428, 1335, 1313, 1262, 1246, 1225, 1188, 1168, 1152, 1114, 1022, 999, 974, 898, 771, 738, 708, 695 cm^{-1} ; MS (EI): m/z (%): 680 (8) [M - bipy]⁺, 603 (7), 524 (6), 448 (16), 276 (15), 199 (28), 156 (100) [bipy]⁺, 155 (43), 128 (20), 78 (17), 40 (22); HRMS (ESI⁺): m/z : calcd. for $\text{C}_{46}\text{H}_{38}\text{MoN}_2\text{O}_4\text{Si}_2+\text{Na}$: 859.1337; found.: 859.1322.

Alkyldiyne Complexes: The large scale preparation of complexes **8b**, **23b**, **25b**, **28b** and **32** is contained in the main text of this article. The preparation and characterization of complexes **5**, **6**, **26** and **27** [previously thought to be **7**] are described in our previous publication (Supporting Information).¹

[NMe₄][Mo(CO)₅(COPh)] (23a). A 2-L, three-necked, round-bottomed flask was equipped with a magnetic stirring bar, a reflux condenser, a pressure-equalizing dropping funnel fitted with a glass stopper and a gas inlet connected to an Argon-vacuum manifold. The flask was flame-dried under vacuum, then filled with Argon. After evacuating and backfilling with Argon three times, the flask was charged with $\text{Mo}(\text{CO})_6$ (18.0 g, 68.2 mmol) and diethyl ether (1 L). The resulting suspension was stirred at reflux temperature until the $\text{Mo}(\text{CO})_6$ was completely dissolved (ca. 15 min). At this point, a solution of PhLi (1.8 M in dibutylether, 37.9 mL, 68.2 mmol) was added via the dropping funnel over 10 min to the refluxing solution, causing the immediate appearance of a dark orange coloration. Once the addition was complete, reflux was continued for 30 min. The dropping funnel and the reflux condenser were replaced by two glass stoppers and all volatile materials were removed under vacuum (10^{-3} mbar) at room temperature without exposing the contents to air.

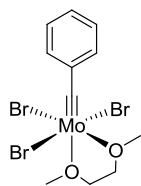
A solution of NMe_4Br (15.8 g, 102.3 mmol) in water (200 mL, not degassed) was quickly added to the residue, causing the precipitation of an orange solid. The resulting suspension was stirred for 15 min in air before the orange solid was filtered off and washed with hexanes (100 mL). The solid was dried under vacuum (10^{-3} mbar) for 4 h to remove the water. The remaining orange material was suspended in CH_2Cl_2 (300 mL) and the mixture was filtered. Addition of diethyl ether (600 mL) to the filtrate caused precipitation of an orange solid, which was filtered off and dried under vacuum (10^{-3} mbar) to afford complex **23a** as a pale orange microcrystalline solid (18.1 g, 64%). The NMR spectra show two distinct signal sets (major:minor isomer, ca. 90:10): ^1H NMR (400 MHz, CD_2Cl_2): major isomer: δ = 7.44 (dd, J = 8.2, 1.4 Hz, 2H), 7.36 (tt, J = 7.2, 1.4 Hz, 2H), 7.23 (tt, J = 7.2, 1.4 Hz, 1H), 3.21 (s,

12H); minor isomer: 7.78 (dd, $J = 7.7, 1.4$ Hz, 2H), 6.87 (tt, $J = 7.1, 1.5$ Hz, 2H), 6.78 (tt, $J = 7.1, 1.5$ Hz, 1H), 3.21 (s, 12H); ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta = 298.2, 218.6, 212.8, 211.7, 201.6, 170.9, 156.1, 146.7, 128.7, 128.4, 127.9, 126.2, 125.0, 121.7, 56.5$ (t, $J = 4$ Hz); IR (neat, cm^{-1}): 3032, 2046, 1946, 1856, 1575, 1509, 1485, 1466, 1417, 1294, 1121, 1071, 947, 835, 762, 698, 656.

[NMe₄][Mo(CO)₅(COAr) (Ar = 4-(Trifluoromethyl)phenyl) (23c). Prepared analogously as an orange solid (3.12 g, 65%). The NMR spectra show two distinct signal sets (major:minor isomer, ca. 95:5): ^1H NMR (400 MHz, CD_2Cl_2): major isomer: $\delta = 7.59$ (d, $J = 8.0$ Hz, 2H), 7.42 (d, $J = 8.0$ Hz, 2H), 3.35 (s, 12H); minor isomer: 7.96 (d, $J = 7.3$ Hz, 2H), 7.07 (d, $J = 7.3$ Hz, 2H), 3.35 (s, 12H); ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta = 298.9, 218.4, 212.0, 211.1, 201.1, 184.7, 181.7, 159.5, 146.2, 130.4, 129.2, 129.1$ (q, $J = 32$ Hz), 127.7 (q, $J = 270$ Hz), 126.4, 125.1 (q, $J = 3.8$ Hz), 124.3, 123.7, 123.4 (q, $J = 32$ Hz), 120.9 (q, $J = 3.8$ Hz), 56.7 (t, $J = 4$ Hz); ^{19}F NMR (75 MHz, CD_2Cl_2): $\delta = -62.3$; IR (neat, cm^{-1}): 3026, 2052, 1961, 1856, 1607, 1566, 1518, 1487, 1371, 1321, 1158, 1117, 1062, 1012, 945, 833, 766, 706.

[NMe₄][Mo(CO)₅(COAr) (Ar = 2,6-Dimethylphenyl) (23d). Prepared analogously as a yellow solid (4.20 g, 63%). ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 6.88$ -6.82 (m, 3H), 3.22 (s, 12H), 2.17 (s, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta = 312.5, 218.3, 211.1, 201.6, 161.2, 138.2, 130.2, 128.4, 128.2, 127.5, 126.3, 124.7, 56.5$ (t, $J = 4$ Hz), 18.5; IR (neat, cm^{-1}): 3020, 2046, 1955, 1862, 1714, 1546, 1517, 1483, 1416, 1374, 947, 826, 766, 691.

[Mo($\equiv\text{CPh}$)Br₃(dme)] (25a). A 1-L, two-necked, round-bottomed flask was equipped with a magnetic stirring bar, a pressure-equalizing dropping funnel fitted with a glass stopper and a gas inlet connected to an Argon-vacuum manifold. The flask was flame-dried under vacuum, then filled with Argon. After evacuating and backfilling with Argon three times, the flask was charged with [NMe₄][Mo(CO)₅(COPh)] (10.0 g, 24.1 mmol) and CH_2Cl_2 (800 mL) under Argon.



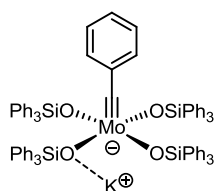
The flask was immersed into a dry ice-acetone bath (-78°C) and the mixture stirred for 15 min before a solution of oxalyl bromide (2.33 mL, 24.8 mmol) in CH_2Cl_2 (5 mL) was added over 10 min, causing a color change from orange to purple and the evolution of gas. Once the addition was complete, stirring was continued for 15 min at -78°C before the mixture was allowed to warm until a sudden color change to yellow was observed (at ca. -30°C). At this point, the mixture was cooled again to -78°C and quickly filtered under Ar through a pad of Celite (5 cm) at this temperature, using a frit (porosity grade 4) jacketed with a cooling mantle connected to a cryostat set to -78°C . 1,2-Dimethoxyethane (dme, 12.5 mL, 120.5 mmol) was added to the resulting pale yellow filtrate at -78°C before a solution of Br_2 (1.26 mL, 24.8 mmol) in CH_2Cl_2 (5 mL) was slowly added at this temperature over a period of 10 min, causing a gentle evolution of gas. Once the addition was complete, the mixture was stirred for 15 min. The then intensely green colored mixture was allowed to reach ambient temperature over the course of 1 h, whereby the color changes from green to yellow-brown. The reaction mixture was stirred for 1 h at room temperature before the dropping funnel was replaced by a distillation head and the solvent was distilled off under vacuum (10^{-3} mbar). The residue was dissolved in CH_2Cl_2 (120 mL) under Argon and the product precipitated upon addition of pentanes (600 mL). The supernatant was removed via cannula under Argon and the residue suspended in CH_2Cl_2 (120 mL). The resulting mixture was filtered under Argon, and the filtrate treated again with pentanes (600 mL), causing the precipitation of the product. The resulting solid was collected under Argon and dried in vacuo (10^{-3} mbar) to give [Mo($\equiv\text{CPh}$)Br₃(dme)] (25a) as a brown crystalline solid (6.2 g, 50%). ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 7.55$ -7.48 (m, 4H), 7.21 (tt, $J = 7.2, 1.6$ Hz, 1H), 4.06 (br s, 2H),

4.04 (br s, 2H), 3.95 (s, 3H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 330.7, 140.4, 131.9, 131.7, 77.6, 71.1, 69.4, 58.0; elemental analysis (%) calcd for $\text{C}_{11}\text{H}_{15}\text{Br}_3\text{MoO}_2$: C 25.66, H 2.94; found: C 25.42, H 2.99.

[Mo($\equiv\text{CAr}$)Br₃(dme)] (Ar = 4-(Trifluoromethyl)phenyl) (25c). Prepared analogously as a green crystalline solid (1.66 g, 71 %). ^1H NMR (400 MHz, CD_2Cl_2): δ = 7.80 (d, J = 8.1 Hz, 2H), 7.64 (d, J = 8.1 Hz, 2H), 4.09 (br s, 2H), 4.03 (br s, 2H), 3.99 (s, 3H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 327.3, 142.9, 133.6 (q, J = 32 Hz), 133.1, 125.1 (q, J = 3.8 Hz), 124.8 (q, J = 272 Hz), 78.5, 73.0, 70.4, 60.8; ^{19}F NMR (75 MHz, CD_2Cl_2): δ = -63.20.

[Mo($\equiv\text{CAr}$)Br₃(dme)] (Ar = 2,6-Dimethylphenyl) (25d). Prepared analogously as a red-brown crystalline solid (927 mg, 85%). ^1H NMR (400 MHz, CD_2Cl_2): δ = 7.09 (d, J = 7.7 Hz, 2H), 6.79 (t, J = 7.6 Hz, 1H), 4.03 (s, 4H), 3.95 (s, 3H), 3.88 (s, 3H), 3.24 (s, 6H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 339.7, 146.2, 140.5, 132.3, 127.0, 78.8, 73.7, 70.1, 60.5, 20.9.

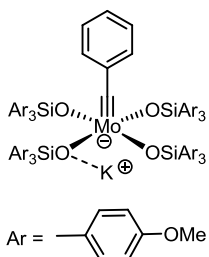
[(Ph₃SiO)₄Mo \equiv CPh][K] (28a). A 500-mL, two-necked, round-bottomed flask was equipped



with a magnetic stirring bar, a pressure-equalizing dropping funnel fitted with a glass stopper and a gas inlet connected to an Argon-vacuum manifold. The flask was flame-dried under vacuum, then filled with Argon. After evacuating and backfilling with Argon three times, the flask was charged with [Mo($\equiv\text{CPh}$)Br₃(dme)] (**25a**) (2.76 g, 5.36 mmol) and toluene (100 mL). The suspension was cooled to 0°C with an ice bath

before a solution of Ph₃SiOK (8.43 g, 26.8 mmol) in toluene (150 mL) was added over 10 min, causing a color change from yellow-brown to purple. The ice bath was removed and the mixture stirred at room temperature for 2 h before it was filtered through a pad of Celite under Argon. The solvent was distilled off under vacuum (10^{-3} mbar) and the residue dissolved in diethyl ether (150 mL). After stirring for 15 min at room temperature, pentanes (150 mL) were added and the precipitate was filtered off under Argon. The purple solid was suspended in CH_2Cl_2 (50 mL) and all insoluble residues were filtered off under Argon. Pentanes (500 mL) were added to the filtrate and the resulting suspension was cooled to -78°C for 1 h. The precipitate was filtered off under Argon and dried in vacuo (10^{-3} mbar) to give complex **28a** as a purple solid (4.41 g, 62%). ^1H NMR (400 MHz, CD_2Cl_2): δ = 7.49 (d, J = 6.6 Hz, 24H), 7.21 (tt, J = 7.4, 1.3 Hz, 12H), 6.95 (t, J = 7.7 Hz, 24H), 6.81-7.79 (m, 3H), 6.13-6.11 (m, 2H), ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 282.9, 144.6, 139.5, 136.4, 130.4, 129.1, 127.7, 127.3, 127.0; elemental analysis (%) calcd for $\text{C}_{79}\text{H}_{65}\text{KMoO}_4\text{Si}_4$: C 71.57, H 4.94; found: C 70.99, H 4.87.

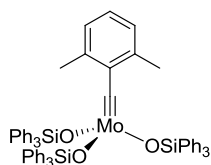
[(Ar₃SiO)₄Mo \equiv CPh][K] (Ar = 4-Methoxyphenyl) (37). A solution of Ar₃SiOK (Ar = 4-



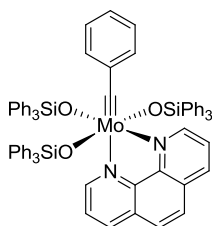
methoxyphenyl, 306 mg, 0.76 mmol) in toluene (2 mL) was added to a solution of [Mo($\equiv\text{CPh}$)Br₃(dme)] (**25a**) (78 mg, 0.15 mmol) in toluene (3 mL). The mixture was stirred at room temperature for 2 h before it is filtered through a pad of Celite under Argon. The solvent was distilled off under vacuum (10^{-3} mbar) and the residue dissolved in diethyl ether (2 mL). After stirring for 15 min at room temperature, pentanes (2 mL) were added to the suspension and the precipitate was filtered off under Argon. The purple solid was suspended in CH_2Cl_2 (1 mL) and all insoluble

residues were filtered off under Argon. Pentanes (3 mL) were added to the filtrate, the precipitate was filtered off under Argon and dried in vacuo (10^{-3} mbar) to give complex **37** as a purple solid (163 mg, 64%). ^1H NMR (400 MHz, CD_2Cl_2): δ = 7.40 (d, J = 8.6 Hz, 24H), 6.82-6.79 (m, 3H), 6.51 (d, J = 8.6 Hz, 24H), 6.10 (dd, J = 8.0, 1.8 Hz, 2H), 3.66 (s, 36H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 281.2, 160.5, 144.7, 137.9, 131.2, 130.3, 127.3, 126.7, 113.3, 55.2.

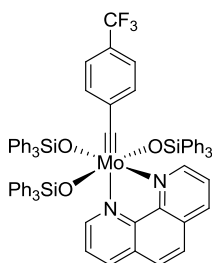
[(Ph₃SiO)₃Mo(≡CAr)] (Ar = 2,6-Dimethylphenyl) (31). A solution of Ph₃SiOK (422 mg, 1.34 mmol) in toluene (2 mL) was added over 1 h to a solution of [Mo(≡CAr)Br₃](dme) (**25d**) (243 mg, 448 μmol) in toluene (3 mL). The mixture was stirred for 1 h before it was filtered through a pad of Celite under Argon. The toluene was removed under vacuum and the residue recrystallized from pentanes (25 mL). The solid material was collected under Argon and dried in vacuo to give complex **31** as a yellow solid (289 mg, 62%). ¹H NMR (400 MHz, CD₂Cl₂): δ = 7.56 (d, *J* = 7.2 Hz, 18H), 7.36 (t, *J* = 7.8 Hz, 9H), 7.21 (t, *J* = 7.4 Hz, 18H), 6.64 (t, *J* = 7.6 Hz, 1H), 6.55 (dd, *J* = 7.6, 0.6 Hz, 2H), 1.71 (s, 6H); ¹³C NMR (100 MHz, CD₂Cl₂): δ = 307.3, 144.7, 139.6, 136.7, 136.5, 136.0, 135.8, 135.5, 135.4, 135.2, 130.5, 130.3, 129.8, 128.7, 128.3, 128.1, 127.7, 127.2, 126.1, 20.2.



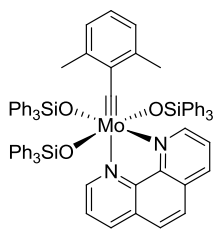
[(Ph₃SiO)₃Mo≡CPh](phen) (8a). A 1-L, two-necked, round-bottomed flask was equipped with a magnetic stirring bar, a glass stopper and a gas inlet connected to an Argon-vacuum manifold. The flask was flame-dried under vacuum, then filled with Argon. After evacuating and backfilling with Argon three times, the flask was charged with complex **28a** (3.83 g, 2.89 mmol) and CH₂Cl₂ (100 mL). 1,10-Phenanthroline (521 mg, 2.89 mmol) was added and the mixture stirred for 5 h at room temperature. Pentanes (400 mL) were added, causing the precipitation of a purple solid which was filtered off under Argon. The solid was dissolved in CH₂Cl₂ (100 mL) and precipitated again upon addition of pentanes (400 mL). The product thus formed was filtered off under Argon and dried in vacuo (10⁻³ mbar) to give complex **8a** as a purple solid (3.10 g, 90%). ¹H NMR (400 MHz, CD₂Cl₂): δ = 9.27 (dd, *J* = 4.6, 1.6 Hz, 1H), 8.90 (dd, *J* = 5.0, 1.6 Hz, 1H), 8.33 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.89 (dd, *J* = 8.0, 1.4 Hz, 6H), 7.82 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.74 (d, *J* = 8.8 Hz, 1H), 7.61 (dd, *J* = 8.2, 4.6 Hz, 1H), 7.53 (d, *J* = 8.8 Hz, 1H), 7.19 (tt, *J* = 7.5, 1.4 Hz, 3H), 7.07 (tt, *J* = 7.5, 1.4 Hz, 6H), 7.03 (dd, *J* = 8.0, 1.4 Hz, 12H), 6.97-6.93 (m, 8H), 6.87 (tt, *J* = 7.5, 1.3 Hz, 1H), 6.80 (t, *J* = 7.7 Hz, 13H), 6.40 (dd, *J* = 8.4, 1.4 Hz, 2H); ¹³C NMR (100 MHz, CD₂Cl₂): δ = 292.3, 155.5, 147.5, 143.7, 143.2, 142.7, 139.4, 138.9, 138.2, 137.2, 136.3, 135.3, 131.2, 130.0, 129.7, 129.2, 128.7, 127.8, 127.3, 127.2, 127.1, 126.7, 124.3, 124.0; IR (film): ν = 3065, 3047, 3022, 1958, 1895, 1823, 1649, 1625, 1587, 1566, 1516, 1483, 1427, 1381, 1342, 1302, 1260, 1221, 1186, 1141, 1110, 1031, 1017, 998, 927, 867, 836, 754, 739, 725, 696 cm⁻¹; elemental analysis (%) calcd for C₇₃H₅₈MoN₂O₃Si₃: C 73.59, H 4.91, N 2.35; found: C 73.21, H 4.81, N 2.32.



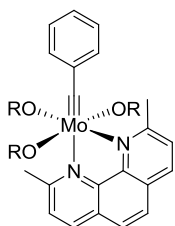
[(Ph₃SiO)₃Mo≡CAr](phen) (Ar = 4-(Trifluoromethyl)phenyl) (8c). Prepared analogously as a purple solid (583 mg, 71%). ¹H NMR (400 MHz, CD₂Cl₂): δ = 9.37 (dd, *J* = 4.6, 1.6 Hz, 1H), 8.83 (dd, *J* = 5.1, 1.6 Hz, 1H), 8.37 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.91 (dd, *J* = 8.0, 1.4 Hz, 6H), 7.84 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.77 (d, *J* = 8.8 Hz, 1H), 7.69 (dd, *J* = 8.2, 4.6 Hz, 1H), 7.55 (d, *J* = 8.8 Hz, 1H), 7.22 (tt, *J* = 7.4, 1.4 Hz, 3H), 7.20 (d, *J* = 7.8 Hz, 2H), 7.10 (tt, *J* = 7.4, 1.4 Hz, 6H), 7.05 (dd, *J* = 8.0, 1.4 Hz, 12H), 6.99 (t, *J* = 7.7 Hz, 6H), 6.84 (t, *J* = 7.7 Hz, 12H), 6.81 (d, *J* = 5.0 Hz, 1H), 6.37 (d, *J* = 7.8 Hz, 2H); ¹³C NMR (100 MHz, CD₂Cl₂): δ = 288.9, 155.4, 147.5, 145.5, 143.2, 142.7, 139.1, 138.6, 138.3, 137.6, 136.3, 135.3, 131.1, 130.1 (q, *J* = 32 Hz), 129.3, 128.8, 127.8, 127.4, 127.3 (q, *J* = 3.8 Hz), 126.0 (q, *J* = 270 Hz), 124.4 (q, *J* = 32 Hz), 124.2 (q, *J* = 3.8 Hz); ¹⁹F NMR (75 MHz, CD₂Cl₂): δ = -62.5; IR (neat, cm⁻¹): 3045, 1958, 1601, 1587, 1515, 1483, 1426, 1327, 1156, 1109, 1064, 1007, 996, 919, 837, 741, 725, 697.



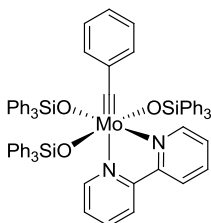
[(Ph₃SiO)₃Mo≡CAr](phen) (Ar = 2,6-Dimethylphenyl) (8d). Prepared analogously as a green solid (146 mg, 73%). ¹H NMR (400 MHz, CD₂Cl₂): = 9.38 (dd, *J* = 5.1, 1.6 Hz, 1H), 8.86 (dd, *J* = 4.6, 1.6 Hz, 1H), 7.99 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.92 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.89 (dd, *J* = 8.0, 1.4 Hz, 6H), 7.59 (d, *J* = 8.8 Hz, 1H), 7.55 (d, *J* = 8.8 Hz, 1H), 7.21 (tt, *J* = 7.5, 1.4 Hz, 3H), 7.18 (dd, *J* = 8.2, 5.0 Hz, 1H), 7.14 (dd, *J* = 8.2, 4.6 Hz, 1H), 7.06-6.99 (m, 12H), 6.85-6.72 (m, 27H), 2.30 (s, 6H); ¹³C NMR (100 MHz, CD₂Cl₂): = 297.9, 156.4, 148.0, 143.4, 142.9, 142.6, 142.4, 139.1, 138.9, 138.8, 137.2, 136.4, 135.5, 135.3, 130.5, 130.3, 130.1, 129.9, 128.4, 128.3, 128.1, 127.7, 127.6, 127.1, 127.0, 126.8, 126.4, 124.2, 124.1, 21.4; IR (neat, cm⁻¹): 3048, 2995, 1588, 1515, 1482, 1426, 1262, 1110, 1017, 999, 932, 836, 739, 695.



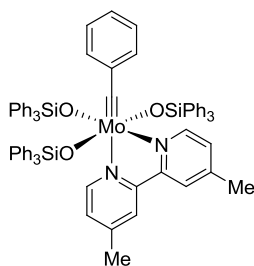
[(Ph₃SiO)₃Mo≡CPh](2,9-dimethyl-1,10-phenanthroline) (33). Prepared analogously as a purple solid (1.12 g, 78%). ¹H NMR (400 MHz, CD₂Cl₂): δ = 8.12 (d, *J* = 8.3 Hz, 1H), 7.72 (dd, *J* = 8.0, 1.3 Hz, 6H), 7.65 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.55 (dd, *J* = 8.4, 4.9 Hz, 2H), 7.40 (d, *J* = 8.3 Hz, 1H), 7.31 (d, *J* = 8.6 Hz, 1H), 7.12 (tt, *J* = 7.4, 1.4 Hz, 8H), 7.09 (dd, *J* = 8.0, 1.3 Hz, 12H), 6.89 (t, *J* = 7.7 Hz, 12H), 6.84 (t, *J* = 7.7 Hz, 6H), 6.76 (t, *J* = 8.2 Hz, 1H), 6.72-6.69 (m, 3H), 6.19-6.17 (m, 2H), 2.86 (s, 3H), 2.64 (s, 3H); ¹³C NMR (100 MHz, CD₂Cl₂): δ = 295.4, 163.4, 161.2, 145.0, 144.9, 144.6, 138.9, 138.8, 137.5, 136.7, 135.6, 135.8, 135.3, 135.1, 132.0, 130.5, 129.1, 128.8, 128.6, 128.4, 128.3, 127.5, 127.4, 126.9, 126.8, 126.2, 126.0, 125.8, 125.6, 32.7, 26.0; IR (neat, cm⁻¹): 3046, 2963, 1587, 1483, 1426, 1260, 1100, 1014, 914, 848, 798, 739, 697.



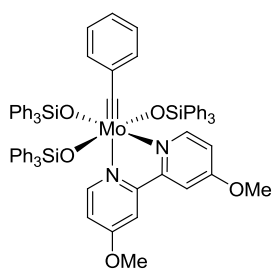
[(Ph₃SiO)₃Mo≡CPh](bipy) (34a). A solution of Ph₃SiOK (2.09 g, 6.64 mmol) in toluene (10 mL) was added to a solution of [Mo(≡CPh)Br₃(dme)] (28a) (855 mg, 1.66 mmol) in toluene (10 mL). After stirring for 1 h, the mixture was filtered and the filtrate added to a solution of 2,2'-bipyridine (259 mg, 1.66 mmol) in toluene (5 mL). After stirring for 1 h, the solvents were evaporated and the residue dissolved in CH₂Cl₂ (5 mL). Pentanes (25 mL) were added, causing the precipitation of a purple solid which was filtered off under Argon. The crude material was dissolved in CH₂Cl₂ (5 mL) and precipitated again upon addition of pentanes (25 mL). The resulting product was collected under Argon and dried in vacuo (10⁻³ mbar) to give complex 34a as a purple solid (1.46 g, 75%). ¹H NMR (400 MHz, CD₂Cl₂): δ = 9.04 (dd, *J* = 5.0, 1.0 Hz, 1H), 8.62 (dd, *J* = 5.4, 1.1 Hz, 1H), 7.87 (dd, *J* = 8.0, 1.4 Hz, 6H), 7.82 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.61 (d, *J* = 8.3 Hz, 1H), 7.36-7.28 (m, 3H), 7.23 (dd, *J* = 7.9, 1.4 Hz, 12H), 7.19 (tt, *J* = 7.5, 1.3 Hz, 3H), 7.15 (tt, *J* = 7.4, 1.3 Hz, 6H), 6.96 (t, *J* = 7.5 Hz, 8H), 6.91 (t, *J* = 7.9 Hz, 12H), 6.85 (tt, *J* = 7.4, 1.3 Hz, 1H), 6.51 (tt, *J* = 7.4, 1.3 Hz, 1H), 6.33 (dd, *J* = 8.3, 1.3 Hz, 2H); ¹³C NMR (100 MHz, CD₂Cl₂): δ = 291.7, 155.7, 151.6, 151.0, 147.6, 143.3, 139.3, 139.0, 138.6, 138.4, 136.1, 135.7, 135.4, 131.1, 130.4, 129.3, 128.7, 128.5, 127.7, 127.4, 127.1, 126.6, 125.4, 125.0, 122.2, 122.1; IR (neat, cm⁻¹): 3045, 1587, 1483, 1468, 1440, 1427, 1310, 1110, 1012, 997, 923, 740, 698; elemental analysis (%) calcd for C₇₁H₅₈MoN₂O₃Si₃: C 73.05, H 5.01, N 2.40; found: C 72.87, H 5.07, N 2.38.



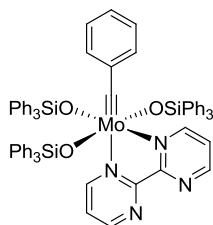
[(Ph₃SiO)₃Mo≡CPh](4,4'-dimethyl-2,2'-bipyridyl) (34b). Prepared analogously as a purple solid (83 mg, 78%). ¹H NMR (400 MHz, CD₂Cl₂): δ = 8.86 (d, *J* = 5.2 Hz, 1H), 8.47 (d, *J* = 5.6 Hz, 1H), 7.87 (dd, *J* = 8.0, 1.4 Hz, 6H), 7.36 (br s, 1H), 7.24 (dd, *J* = 8.0, 1.4 Hz, 12H), 7.18 (tt, *J* = 7.5, 1.4 Hz, 3H), 7.15 (tt, *J* = 7.5, 1.4 Hz, 6H), 7.12 (d, *J* = 5.2 Hz, 1H), 7.04 (m, 1H), 6.95 (t, *J* = 7.8 Hz, 8H), 6.91 (t, *J* = 7.8 Hz, 12H), 6.83 (tt, *J* = 7.4, 1.3 Hz, 2H), 6.35 (dd, *J* = 8.4, 1.4 Hz, 2H), 6.29-6.27 (m, 1H), 2.43 (s, 3H), 2.18 (s, 3H); ¹³C NMR (100 MHz, CD₂Cl₂): δ = 291.5, 155.2, 151.7, 151.0, 150.5, 150.1, 147.4, 143.5, 139.5, 139.3, 136.3, 135.9, 135.7, 135.3, 131.3, 130.5, 129.1, 128.6, 128.3, 127.7, 127.3, 127.1, 126.6, 126.1, 125.7, 125.0, 122.9, 21.6, 21.4; IR (neat, cm⁻¹): 3065, 1610, 1587, 1483, 1285, 1109, 1013, 997, 927, 831, 742, 698.



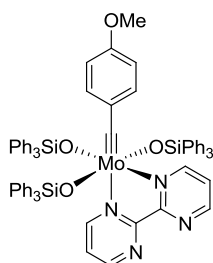
[(Ph₃SiO)₃Mo≡CPh](4,4'-dimethoxy-2,2'-bipyridyl) (34c). Prepared analogously as a purple solid (78 mg, 71%). ¹H NMR (400 MHz, CD₂Cl₂): δ = 8.81 (d, *J* = 5.9 Hz, 1H), 8.41 (d, *J* = 6.4 Hz, 1H), 7.86 (dd, *J* = 8.1, 1.4 Hz, 6H), 7.27 (dd, *J* = 8.1, 1.5 Hz, 12H), 7.18 (tt, *J* = 7.5, 1.4 Hz, 3H), 7.14 (tt, *J* = 7.5, 1.4 Hz, 6H), 6.99 (d, *J* = 2.3 Hz, 1H), 6.95-6.90 (m, 20H), 6.82 (tt, *J* = 7.4, 1.2 Hz, 1H), 6.78 (dd, *J* = 5.9, 2.4 Hz, 1H), 6.65 (d, *J* = 2.7 Hz, 1H), 6.32 (dd, *J* = 8.3, 1.2 Hz, 2H), 5.91 (dd, *J* = 6.5, 2.6 Hz, 1H), 3.90 (s, 3H), 3.74 (s, 3H); ¹³C NMR (100 MHz, CD₂Cl₂): δ = 290.1, 167.4, 166.7, 157.0, 153.2, 152.5, 149.0, 139.4, 139.3, 136.2, 135.8, 135.2, 131.2, 130.4, 129.0, 128.6, 128.5, 128.2, 127.6, 127.3, 127.1, 126.5, 109.8, 109.6, 109.0, 66.0, 15.5; IR (neat, cm⁻¹): 3064, 1600, 1564, 1483, 1427, 1329, 1252, 1111, 1024, 1014, 932, 835, 743, 701.



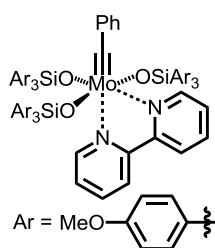
[(Ph₃SiO)₃Mo≡CPh](2,2'-bispyrimidine) (35a). Prepared analogously as a purple solid (97 mg, 69%). ¹H NMR (400 MHz, CD₂Cl₂): δ = 9.02 (br s, 2H), 8.46 (dd, *J* = 4.8, 2.3 Hz, 1H), 8.31 (dd, *J* = 5.5, 2.3 Hz, 1H), 7.85 (dd, *J* = 7.9, 1.3 Hz, 6H), 7.39 (t, *J* = 5.0 Hz, 1H), 7.25-7.15 (m, 21H), 6.99-6.93 (m, 19H), 6.91-6.87 (m, 2H), 6.28 (dd, *J* = 6.8, 1.5 Hz, 2H), 6.17 (t, *J* = 5.1 Hz, 1H); ¹³C NMR (100 MHz, CD₂Cl₂): δ = 292.7, 160.6, 159.6, 159.1, 158.9, 158.4, 157.6, 154.6, 143.6, 138.9, 138.5, 136.0, 135.5, 131.0, 130.3, 129.5, 129.1, 128.1, 127.9, 127.7, 127.3, 127.2, 122.6, 122.0; IR (neat, cm⁻¹): 3067, 1738, 1588, 1567, 1484, 1427, 1405, 1115, 1028, 1016, 997, 926, 835, 758, 738, 710, 696, 657.



[(Ph₃SiO)₃Mo≡CAr](2,2'-bispyrimidine) (35b) (Ar = 4-Methoxyphenyl). Prepared analogously as a green solid (97 mg, 75%). ¹H NMR (400 MHz, CD₂Cl₂): δ = 9.03 (d, *J* = 5.0 Hz, 2H), 8.46 (dd, *J* = 4.8, 2.4 Hz, 1H), 8.31 (dd, *J* = 5.4, 2.4 Hz, 1H), 7.85 (dd, *J* = 8.0, 1.4 Hz, 6H), 7.39 (t, *J* = 5.0 Hz, 1H), 7.24 (dd, *J* = 8.0, 1.4 Hz, 12H), 7.21 (tt, *J* = 7.5, 1.3 Hz, 3H), 7.17 (tt, *J* = 7.5, 1.4 Hz, 6H), 6.98-6.92 (m, 18H), 6.43 (d, *J* = 8.9 Hz, 2H), 6.22 (d, *J* = 8.9 Hz, 2H), 6.17 (t, *J* = 5.0 Hz, 1H), 3.74 (s, 3H); ¹³C NMR (100 MHz, CD₂Cl₂): δ = 292.7, 160.5, 159.6, 159.2, 158.9, 158.4, 158.1, 157.6, 154.6, 139.0, 138.6, 137.8, 136.0, 135.5, 135.3, 132.9, 130.5, 129.4, 129.0, 128.3, 127.9, 127.7, 122.5, 121.9, 112.5, 55.5; IR (neat, cm⁻¹): 3066, 1738, 1588, 1568, 1556, 1499, 1483, 1427, 1403, 1278, 1244, 1184, 1111, 1030, 1010, 997, 911, 839, 760, 738, 697, 654.



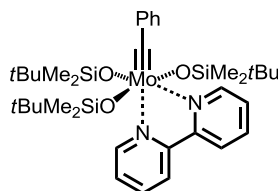
[(Ar₃SiO)₃Mo≡CPh](bipy) (Ar = 4-Methoxyphenyl) (38). A mixture of complex **25a** (0.21 g, 0.40 mmol) and potassium tris(*p*-methoxyphenyl)silanolate (0.65 g, 1.60 mmol) in toluene (10 mL) was stirred for 1 h at ambient temperature.



After filtration under Argon, a solution of bipyridine (0.13 g, 0.80 mmol) in Et₂O (10 mL) was added to the filtrate and the resulting mixture was stirred for 2 h. The solvents were removed under reduced pressure, and Et₂O (30 mL) was added to the residue to afford a purple solution and a black sticky precipitate. After filtration under Argon, the filtrate was

evaporated to provide a purple solid, which was recrystallized from CH₂Cl₂/pentane (0.21 g, 36%). ¹H NMR (400 MHz, CD₂Cl₂): δ = 9.00 (ddd, *J* = 5.0, 1.7, 0.8 Hz, 1H), 8.69 (ddd, *J* = 5.4, 1.6, 0.6 Hz, 1H), 7.86 (ddd, 7.8, 7.8, 1.8 Hz, 1H), 7.72 (d, *J* = 8.6 Hz, 6H), 7.67 (d, *J* = 8.3 Hz, 1H), 7.44–7.29 (m, 3H), 7.11 (d, *J* = 8.6 Hz, 12H), 6.94 (dd, *J* = 7.4, 7.4 Hz, 2H), 6.84 (tt, *J* = 7.4, 1.3 Hz, 1H), 6.62 (ddd, *J* = 7.2, 5.4, 1.5 Hz, 1H), 6.47 (d, *J* = 8.6 Hz, 6H), 6.45 (d, *J* = 8.6 Hz, 12H), 6.29 (dd, 7.4, 1.3 Hz, 2H), 3.68 (s, 18H), 3.62 (s, 9H); ¹³C NMR (100 MHz, CD₂Cl₂): δ = 291.01, 160.87, 160.60, 156.18, 152.01, 151.51, 148.02, 143.81, 138.49, 138.47, 137.92, 137.27, 131.47, 131.31, 131.04, 127.26, 126.62, 125.44, 125.19, 122.30, 122.26, 113.57, 113.29, 55.39, 55.29.

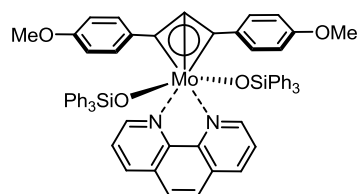
[(*t*BuMe₂SiO)₃Mo≡CPh](bipy) (39). A mixture of complex **25a** (0.21 g, 0.40 mmol) and potassium *tert*-butyldimethylsilanolate (0.20 g, 1.20 mmol) in toluene (8 mL) was stirred for 1.5 h at ambient temperature. After filtration under Argon, a solution of bipyridine (0.13 g, 0.40 mmol) in toluene (2 mL) was added to the filtrate and the resulting mixture stirred for 2 h.



The solvent was evaporated, the residue was triturated with Et₂O and pentane, and then the solvent was removed again. The residue was

dissolved in pentane (3 mL) and the resulting solution was cooled to –20 °C to cause crystallization of the product. Because of the very high solubility of the product in pentane even at ≤ –20 °C, only small amounts of crystalline **39** could be obtained, which were only characterized by X-ray diffraction (see above).

Deprotiometalacycle 43. ¹H NMR (400 MHz, CD₂Cl₂): = 10.26 (dd, *J* = 4.8, 1.5 Hz, 2H), 8.32



(dd, *J* = 8.1, 1.5 Hz, 2H), 8.00 (d, *J* = 8.7 Hz, 4H), 7.74 (s, 2H), 7.71 (dd, *J* = 8.1, 4.8 Hz, 2H), 7.19 (d, *J* = 8.7 Hz, 4H), 7.03 (tt, *J* = 7.4, 1.3 Hz, 6H), 6.78 (t, *J* = 7.7 Hz, 12H), 6.49 (dd, *J* = 7.9, 1.3 Hz, 12H), 3.99 (s, 6H); ¹³C NMR (100 MHz, CD₂Cl₂): = 205.3, 190.6, 158.9, 152.3, 145.0, 138.6, 137.6, 136.5, 136.0, 135.6, 135.4, 135.3, 134.9, 134.6, 132.7, 130.4, 128.6, 127.6, 127.5,

127.3, 127.1, 124.6, 114.2, 55.8.

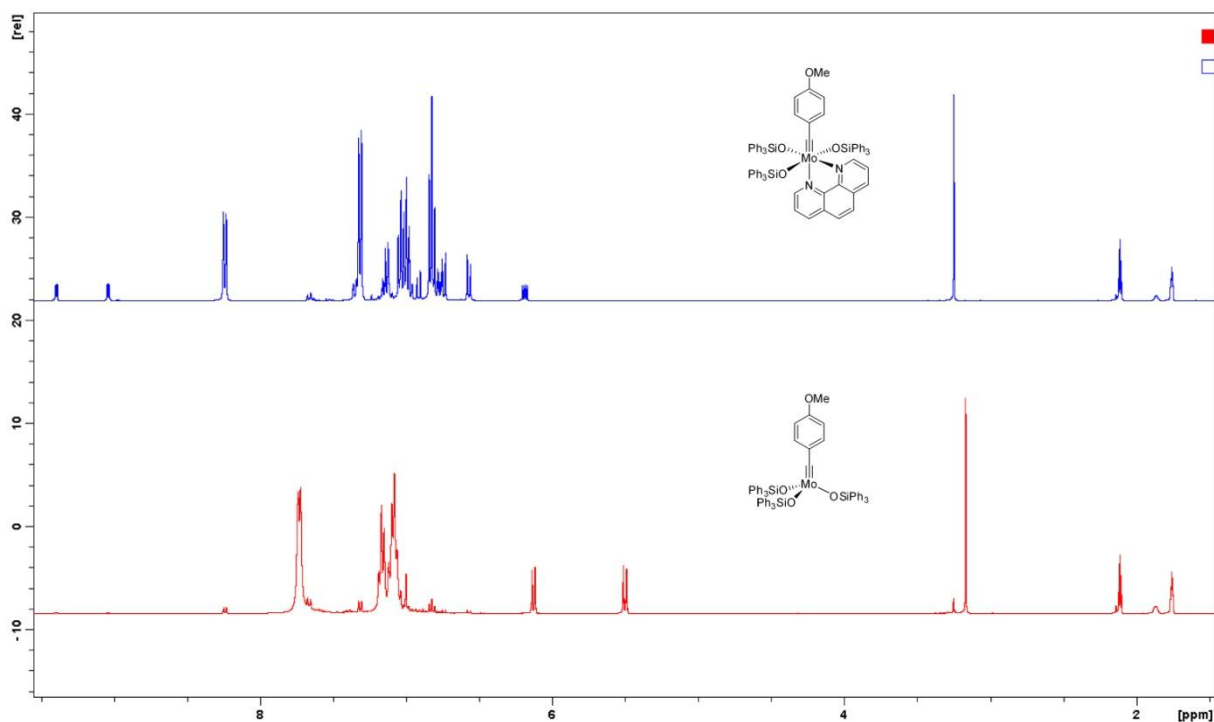


Figure S9. The activation of the 1,10-phenanthroline adducts by metal salts can be readily monitored by ^1H NMR (CD_2Cl_2) due to the characteristic shift differences between precatalysts such as $[\text{Mo}(\equiv\text{CAr})(\text{OSiPh}_3)_3(\text{phen})]$ (**8b**) and the corresponding donor free complex $[\text{Mo}(\equiv\text{CAr})(\text{OSiPh}_3)_3]$ (**32**); Ar = 4-methoxyphenyl.

Alkyne Metathesis Reactions

Representative Alkyne Metathesis Reaction using Complex $[(\text{Ph}_3\text{SiO})_4\text{Mo}\equiv\text{CPh}][\text{K}\cdot(\text{Et}_2\text{O})]$ (27a**)³ (Table 2, entry 2): 1,2-Bis(2-methoxyphenyl)ethyne.** A suspension containing 1-methoxy-2-(prop-1-yl)benzene (146 mg, 1 mmol), complex **27a** (22 mg, 0.02 mmol, 2 mol%)³ and powdered MS 5 \AA (1 g) in toluene (5 mL) was stirred for 2 h at ambient temperature before the mixture was filtered through a short plug of silica. The filtrate was evaporated and the residue purified by flash chromatography (hexanes/EtOAc, 20:1) to give 1,2-bis(2-methoxyphenyl)ethyne as a colorless solid (115 mg, 97%). M. p. = 126–127°C; ^1H NMR (400 MHz, CD_2Cl_2): δ = 7.49 (ddd, J = 7.3, 1.6, 0.5 Hz, 2H), 7.33 (ddd, J = 7.9, 7.7, 1.9 Hz, 2H), 6.95 (td J = 7.9, 1.0 Hz, 4H), 3.92 (s, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 160.3 (2xC), 133.7 (2xCH), 130.1 (2xCH), 120.8 (2xCH), 113.0 (2xC), 111.3 (2xCH), 90.1 (2xC), 56.2 (2xCH₃); IR (film): $\tilde{\nu}$ = 3105, 3033, 2998, 2963, 2937, 2833, 1945, 1903, 1863, 1598, 1574, 1498, 1464,

3 This complex was previously (ref. 1) thought to be the neutral Et_2O adduct $[(\text{Ph}_3\text{SiO})_3\text{Mo}\equiv\text{CPh}](\text{Et}_2\text{O})$ (**7**); for the reassignment of the constitution of this complex, see the main text of this article.

1456, 1432, 1274, 1241, 1184, 1162, 1115, 1047, 1020, 937, 750 cm^{-1} ; MS (EI) m/z (%): 238 [M^+] (100), 237 (32), 223 (23), 221 (15), 207 (10), 195 (5), 178 (8), 165 (14), 152 (9), 131 (19), 111 (6), 97 (3), 89 (3); HRMS (ESI): m/z : calcd for $\text{C}_{16}\text{H}_{14}\text{O}_2 + \text{Na}$: 261.0886; found: 261.0884.

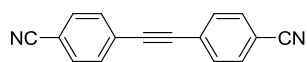
Representative Alkyne Metathesis Reaction using $[(\text{Ph}_3\text{SiO})_4\text{Mo}\equiv\text{C}\text{Ar}][\text{K}]$ (Ar = 4-Methoxyphenyl) (28b) (Table 4, entry 3). A flame-dried flask was charged under Argon with 1,6-bis(pent-3-yn-1-yl) hexanedioate (1.83 g, 6.57 mmol), molecular sieves powder (MS 5Å, 13 g) and toluene (400 mL). The resulting suspension was stirred for 30 min before complex **28b** (269 mg, 0.203 mmol) was added. After stirring for 16 h at ambient temperature, the mixture was filtered through a pad of Celite, which was carefully rinsed with ethyl acetate (500 mL). The combined filtrates were evaporated, the residue suspended in ethyl acetate (8 mL) and the resulting mixture stirred at reflux temperature until a clear solution has formed. The heating bath was removed and the solution allowed to reach ambient temperature. After standing overnight, the precipitated crystals were filtered off, rinsed with hexanes and dried in vacuum to give a first crop of 1,8-dioxacyclotetradec-11-yne-2,7-dione (950 mg). The filtrate from the recrystallization was evaporated and the residue purified by flash chromatography (hexanes/ethyl acetate, 4:1) to give a second crop of the product (300 mg). 1,8-Dioxacyclotetradec-11-yne-2,7-dione was obtained in form of colorless crystals (1.25 g, 84% overall). m. p. = 109–110°C; ^1H NMR (400 MHz, CD_2Cl_2): δ = 4.13–4.06 (m, 4H), 2.53–2.47 (m, 4H), 2.39–2.30 (m, 4H), 1.76–1.67 (m, 4H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 173.2 (2xC), 78.2 (2xC), 62.8 (2x CH_2), 35.2 (2x CH_2), 25.4 (2x CH_2), 19.4 (2x CH_2); IR (film) $\tilde{\nu}$ = 2995, 2954, 2937, 2918, 2901, 2872, 1721, 1458, 1425, 1384, 1341, 1272, 1236, 1167, 1140, 1080, 1065, 1021, 981, 931, 843, 824, 699 cm^{-1} ; MS (EI) m/z (%): 129 (3), 111 (8), 78 (100), 66 (20), 55 (15), 41 (8); HRMS (ESI): m/z : calcd for $\text{C}_{12}\text{H}_{16}\text{O}_4 + \text{Na}$: 247.0941; found: 247.0938.

Gram-Scale Synthesis of 1,2-Bis(4-(trifluoromethyl)phenyl)ethyne with $[\text{Mo}(\equiv\text{CPh})(\text{OSiPh}_3)_3](\text{phen})$ (8a) Activated with MnCl_2 (Table 2, entry 6). A solution containing $[\text{Mo}(\equiv\text{CPh})(\text{OSiPh}_3)_3](\text{phen})$ (**8a**) (387 mg, 0.33 mmol, 5 mol%) and MnCl_2 (41 mg, 0.33 mmol) in toluene (5 mL) was stirred at 80°C for 30 min. After this activation phase, the mixture was allowed to reach ambient temperature before it was added to a suspension of 1-(prop1-ynyl)-4-(trifluoromethyl)benzene (1.20 g, 6.52 mmol) and powdered MS 5Å (6.5 g) in toluene (28 mL). The resulting mixture was stirred at ambient temperature for 3 h before it was filtered through a short plug of silica. The filtrate was evaporated and the residue purified by flash chromatography (hexanes) to give the desired product as a colorless solid (973 mg, 95%). ^1H NMR (300 MHz, $[\text{D}_8]$ -toluene): δ = 7.26–7.18 (m, 8H); ^{13}C NMR (75 MHz, $[\text{D}_8]$ -toluene): δ = 132.9, 131.6, 131.1, 127.3, 127.3, 126.3, 126.3, 126.2, 123.4, 91.2; ^{19}F NMR (300 MHz, $[\text{D}_8]$ -toluene): δ = –62.8; IR (film): $\tilde{\nu}$ = 2929, 2635, 1934, 1808, 1689, 1636, 1613, 1569, 1523, 1406, 1312, 1171, 1133, 1104, 1062, 1016, 968, 838, 754, 738, 712, 701, 692 cm^{-1} ; MS (EI) m/z (%): 314 [M^+] (100), 295 (18), 264 (9), 245 (5), 225 (7), 194 (2), 176 (3), 132 (2), 107 (2); HRMS (ESI): m/z : calcd for $\text{C}_{16}\text{H}_8\text{F}_6$: 314.0530; found: 314.0530.

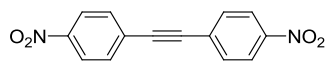
The analytical and spectral data of the products formed following these general procedures can be found in the Supporting Information of our previous publications.^{1,4} The data of compounds not previously described are as follows:

4 a) V. Hickmann, M. Alcarazo, A. Fürstner, *J. Am. Chem. Soc.* **2010**, *132*, 11042–11044; b) V. Hickmann, A. Kondoh, B. Gabor, M. Alcarazo, A. Fürstner, *J. Am. Chem. Soc.* **2011**, *133*, 13471–13480; c) S. Benson, M.-P. Collin, A. Arlt, B. Gabor, R. Goddard, A. Fürstner, *Angew. Chem.* **2011**, *123*, 8898–8903; *Angew. Chem. Int. Ed.* **2011**, *50*, 8739–8744; d) K. Lehr, R. Mariz, L. Leseurre, B. Gabor, A. Fürstner, *Angew. Chem.* **2011**, *123*, 11575–11579; *Angew. Chem. Int. Ed.* **2011**, *50*, 11373–11377; e) A. Fürstner, A. Rumbo, *J. Org. Chem.* **2000**, *65*, 2608–2611.

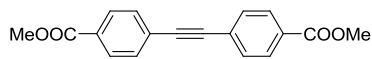
Orange solid. Mp = 252-255°C; ¹H NMR (400 MHz, CDCl₃): δ 8.27 (d, *J* = 8.8 Hz, 4H), 7.73 (d, *J* = 8.8 Hz, 4H); ¹³C NMR (100 MHz, CDCl₃): δ 147.3, 134.6, 132.3, 128.5, 127.6, 123.4 91.6; IR 3058, 2920, 2225, 1928, 1675, 1606, 1502, 1408, 1273, 1182, 1022, 841, 553; MS (EI) *m/z* (%): 228 [M⁺] (100), 201 (8), 175 (4), 151 (3), 137 (1), 100 (3), 87 (4), 74 (3), 63 (1); HRMS (ESI): *m/z*: calcd for C₁₆H₈N₂: 268.0687; found: 228.0688. The analytical and spectroscopic data are in accordance with those reported in the literature.⁵



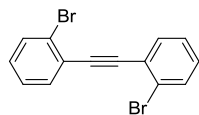
Yellow solid. Mp = 205-207°C; ¹H NMR (400 MHz, CDCl₃): δ 7.68 (d, *J* = 8.5 Hz, 4H), 7.64 (d, *J* = 8.5 Hz, 4H); ¹³C NMR (100 MHz, CDCl₃): δ 132.4, 132.3, 127.2, 118.4, 112.6, 91.7; IR (neat, cm⁻¹): 3058, 2920, 2254, 2225, 1928, 1675, 1606, 1502, 1408, 1273, 1182, 1022, 841, 553; MS (EI) *m/z* (%): 268 [M⁺] (100), 238 (23), 222 (7), 210 (4), 192 (6), 176 (42), 163 (19), 150 (15), 137 (4), 126 (5), 111 (2), 99 (4), 75 (7), 63 (4), 51 (3); HRMS (ESI): *m/z*: calcd for C₁₄H₈N₂O₄: 268.0484; found: 268.0485. The analytical and spectroscopic data are in accordance with those reported in the literature.⁶



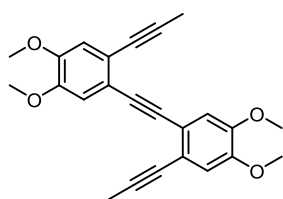
Pale yellow solid. Mp = 224–225°C; ¹H NMR (400 MHz, CDCl₃): δ 8.03 (d, *J* = 8.4 Hz, 4H), 7.59 (d, *J* = 8.5 Hz, 4H), 3.93 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 166.7, 132.0, 130.3, 129.9, 127.7, 91.7, 52.6; IR (film) $\tilde{\nu}$ = 3221, 2959, 1714, 1607, 1428, 1275, 1105, 853, 768, 710 cm⁻¹; MS (EI) *m/z* (%): 294 (100) [M⁺], 263 (96), 176 (22), 116 (18), 102 (13); HRMS (ESI⁺): *m/z*: calcd for C₁₈H₁₄O₄ + Na: 317.0784; found: 317.0787. The analytical and spectroscopic data are in agreement with those reported in the literature.⁷



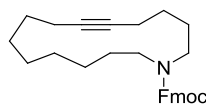
Colorless solid; M. p. = 80–81°C; ¹H NMR (300 MHz, CDCl₃): δ 7.62 (m, 4H), 7.27 (dt, *J* = 7.6, 1.2 Hz, 2H), 7.22 (dt, *J* = 8.0, 1.7 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 134.0, 132.9, 130.1, 127.4, 125.9, 125.5, 92.6; IR (film) $\tilde{\nu}$ = 3043, 1958, 1922, 1592, 1557, 1479, 1434, 1047, 1019, 746, 664 cm⁻¹; MS (EI) *m/z* (%): 336 (100) [M⁺], 176 (65), 88 (28); HRMS (EI): *m/z*: calcd for C₁₄H₈Br₂: 333.8993; found: 333.8993. The analytical and spectroscopic data are in agreement with those reported in the literature.⁷



Yellow solid (114 mg, 61%). Mp = 254-255 °C; ¹H NMR (400 MHz, CDCl₃): δ = 6.98 (s, 2H), 6.91 (s, 2H), 3.89 (s, 6H), 3.88 (s, 6H), 2.12 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ = 148.9, 148.4, 119.5, 118.7, 114.2, 114.2, 90.6, 88.4, 78.5, 55.9, 55.9, 4.6; IR (ATR): 3002, 2965, 2943, 2911, 2844, 1697, 1602, 1536, 1512, 1463, 1445, 1412, 1364, 1279, 1264, 1241, 1232, 1220, 1206, 1186, 1156, 1034, 1010, 957, 856, 811, 741, 711, 698, 673 cm⁻¹; MS (EI): *m/z* (%): 376 (4), 375 (25), 374 (100) [M⁺], 360 (6), 359 (26), 315 (4), 301 (4), 285 (4), 187 (9); HRMS (ESI⁺): *m/z*: calcd for C₂₄H₂₂O₄ + Na: 397.1410; found: 397.1413.



Colorless solid. ¹H NMR (rotamers, 300 MHz, CDCl₃) δ 7.75 (d, 2H, *J* = 7.2 Hz), 7.58 (d, 2H, *J* = 7.2 Hz), 7.41 (m, 4H), 4.56 (d, 1H, *J* = 5.5 Hz), 4.49 (d, 1H, *J* = 5.9 Hz), 4.22 (d, 1H, *J* = 2.4 Hz), 3.28 (d, 1H, *J* = 6.4 Hz), 3.20 (t, 1H, *J* = 8 Hz), 3.12 (t, 1H, *J* = 6.9 Hz), 2.91 (m, 3H), 2.20 (m, 3H), 2.12 (t, 1H, *J* = 6.4 Hz), 1.75 (m, 1H),



5 N. G. Pschirer, U. H. F. Bunz, *Tetrahedron Lett.* **1999**, *40*, 2481-2484.

6 S. Akiyama, K. Tajima, S. Nakatsuji, K. Nakashima, K. Abiru, M. Watanabe, M. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 2043-2051.

7 M. J. Mio, L. C. Kopel, J. B. Braun, T. L. Gadzikwa, K. L. Hull, R. G. Brisbois, C. J. Markworth, P. A. Grieco, *Org. Lett.* **2002**, *4*, 3199-3202.

1.49-1.20 (m, 13H), 1.15 (m, 2H); ^{13}C NMR (rotamers, 75 MHz, CDCl_3) δ 156.3 (s), 156.2 (s), 144.2 (s), 141.4 (d), 127.5 (d), 126.9 (d), 124.8 (d), 124.7 (t), 119.8 (d), 81.0 (s), 80.8 (s), 79.9 (s), 79.8 (s), 66.5 (t), 66.2 (t), 49.8 (t), 49.3 (t), 49.3 (t), 48.6 (t), 47.5 (d), 28.6 (t), 28.1 (t), 28.0 (t), 28.0 (t), 27.6 (t), 27.4 (t), 27.3 (t), 27.0 (t), 26.4 (t), 26.2 (t), 25.6 (t), 24.5 (t), 24.4 (t), 18.3 (t), 18.2 (t), 18.0 (t); IR (neat, cm^{-1}): 2924, 2851, 1696, 1453, 1421, 1381, 1304, 1258, 1177, 1123, 1051, 980, 768, 737; HRMS (ESI+): m/z : calcd for $\text{C}_{29}\text{H}_{35}\text{NO}_2+\text{H}$ 430.274603, found 430.273975. The analytical and spectroscopic data are in accordance with those reported in the literature.⁸