Electronic Supplementary Information

Synthesis of Li/OR phosphinidenoid complexes – on the evidence for intramolecular O-Li donation and the effect of cation encapsulation

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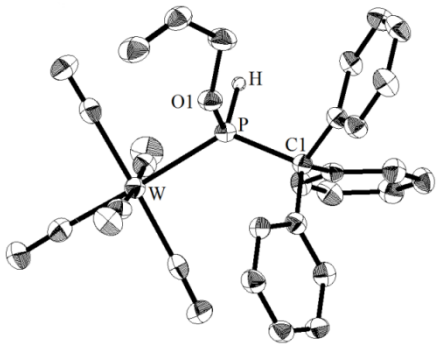
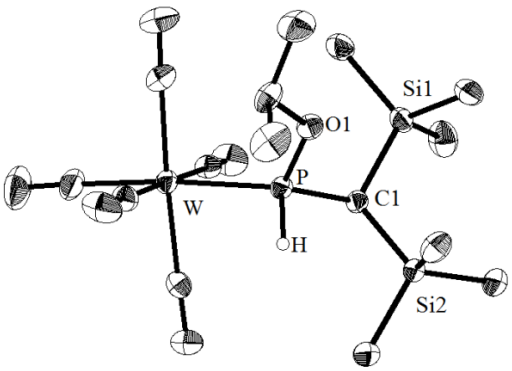
Content:

Crystal structure data of complex 12a ($C_{27}H_{21}O_6PW$): crystal size 0.15 x 0.13 x 0.07 mm, monoclinic, P $2_1/c$, a = 12.1595(2), b = 10.5241(3), c = 19.7949(5) Å, α = 90, β = 97.6003(14), γ = 90°, V = 2510.86(10) $Å^3$, Z = 4, ρ_{calc} = 1.736 Mg m^{-3}, $2\theta_{max}$ = 56°, collected (independent) reflections = 42848 (6035), R_{int} = 0.1325, μ = 4.704 mm^{-1}, 319 refined parameters, 1 restraints, R_1 (for I > 2σ(I)) = 0.0398, *w*R_2 (for all data) = 0.0841, max./min. residual electron density = 2.728/–2.054 e · $Å^{-3}$.



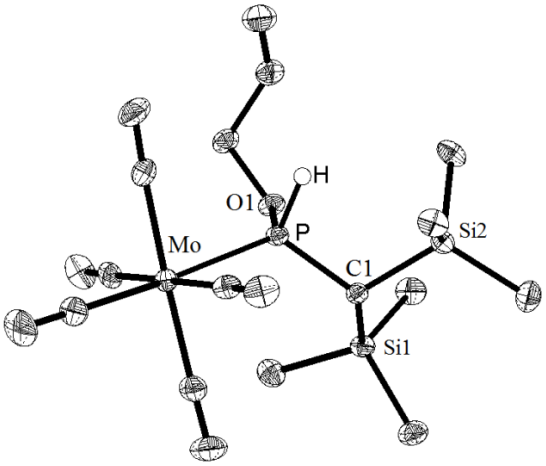
Molecular structure of complex **12a** in the crystal (50% probability level, hydrogen atoms except on P are omitted for clarity). Selected bond lengths [Å] and angles [°]: W–P 2.4993(13), P–C(1) 1.915(4), P–O(1) 1.622(3), P–H 1.38(4), W–P–H 115.2(18), W–P–C(1) 126.3(15), W–P–O(1) 106.66(13), H-P-O(1) 101.2(17), C(1)-P-O(1) 104.83(18), C(1)-P-H 99.6(17).

Crystal structure data of complex 14c ($C_{15}H_{27}O_6PSi_2W$): crystal size 0.12 x 0.04 x 0.04 mm, triclinic, P -1, a = 9.3698(2), b = 10.3785(2), c = 12.2990(2) Å, α = 76.1508(14), β = 85.9396(14), γ = 88.6518(12)°, V = 1158.30(4) $Å^3$, Z = 2, ρ_{calc} = 1.647 Mg m^{-3}, $2\theta_{max}$ = 56°, collected (independent) reflections = 29506 (5556), R_{int} = 0.0724, μ = 5.182 mm^{-1}, 237 refined parameters, 3 restraints, R_1 (for I > 2σ(I)) = 0.0310, *w*R_2 (for all data) = 0.0598, max./min. residual electron density = 1.567/–1.779 e · $Å^{-3}$.



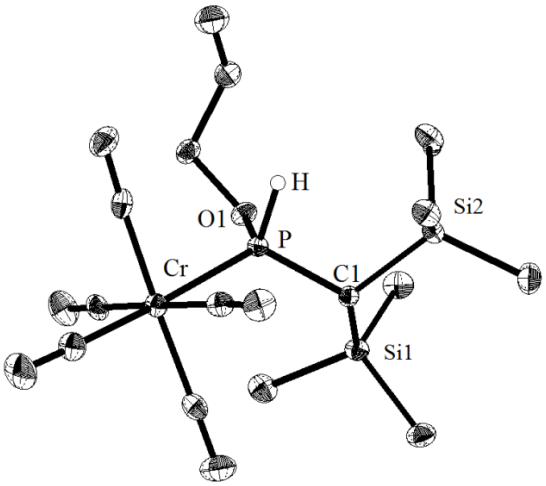
Molecular structure of complex **14c** in the crystal (50% probability level, hydrogen atoms except on P are omitted for clarity). Selected bond lengths [Å] and angles [°]: W–P 2.4816(8), P–C(1) 1.810(3), P–O(1) 1.626(2), P–H 1.43(2), W–P–H 109.1(12), W–P–C(1) 120.11(11), W–P–O(1) 121.33(9), H-P-O(1) 100.7(13), C(1)-P-O(1) 99.70(13), C(1)-P-H 102.9(13).

Crystal structure data of complex 15a ($C_{15}H_{25}O_6PSi_2Mo$): crystal size 0.27 x 0.10 x 0.05 mm, monoclinic, P $2_1/c$, a = 16.6435(7), b = 9.4805(4), c = 14.8822(7) Å, α = 90, β = 106.9120(10), γ = 90°, V = 2246.69(17) Å^3, Z = 4, ρ_{calc} = 1.432 Mg m^{-3}, $2\theta_{max}$ = 56°, collected (independent) reflections = 13098 (5414), R_{int} = 0.0320, μ = 0.786 mm^{-1}, 235 refined parameters, 5 restraints, R_1 (for I > 2σ(I)) = 0.0318, wR_2 (for all data) = 0.0880, max./min. residual electron density = 0.812/–0.958 e · Å^{-3}.



Molecular structure of complex **15a** in the crystal (50% probability level, hydrogen atoms except on P are omitted for clarity). Selected bond lengths [Å] and angles [°]: Mo–P 2.4788(6), P–C(1) 1.812(2), P–O(1) 1.6264(15), P–H 1.30(2), Mo–P–H 111.0(10), Mo–P–C(1) 120.43(7), Mo–P–O(1) 119.70(6), H-P-O(1) 99.0(10), C(1)-P-O(1) 99.71(8), C(1)-P-H 103.9(9).

Crystal structure data of complex 16a ($C_{15}H_{25}O_6PSi_2Cr$): crystal size 0.20 x 0.10 x 0.02 mm, monoclinic, P $2_1/c$, a = 16.500(2), b = 9.2871(12), c = 14.7982(16) Å, α = 90, β = 107.024(3), γ = 90°, V = 2168.3(5) Å^3, Z = 4, ρ_{calc} = 1.349 Mg m^{-3}, $2\theta_{max}$ = 56°, collected (independent) reflections = 23154 (5218), R_{int} = 0.0489, μ = 0.737 mm^{-1}, 235 refined parameters, 10 restraints, R_1 (for I > 2σ(I)) = 0.0358, wR_2 (for all data) = 0.0834, max./min. residual electron density = 0.403/–0.349 e · Å^{-3}.



Molecular structure of complex **16a** in the crystal (50% probability level, hydrogen atoms except on P are omitted for clarity). Selected bond lengths [Å] and angles [°]: Cr–P 2.3281(6),

P–C(1) 1.8084(19), P–O(1) 1.6234(14), P–H 1.308(19), Cr–P–H 109.4(9), Cr–P–C(1) 120.47(7), Cr–P–O(1) 119.48(5), H-P-O(1) 101.8(9), C(1)-P-O(1) 99.80(8), C(1)-P-H 103.3(9).