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:

1. Crystal structure data of complex 12a (C_{27}H_{21}O_{6}PW) ........................................2
2. Crystal structure data of complex 14c (C_{15}H_{27}O_{6}PSi_{2}W) ....................................2
3. Crystal structure data of complex 15a (C_{15}H_{25}O_{6}PSi_{2}Mo) .................................3
4. Crystal structure data of complex 16a (C_{15}H_{25}O_{6}PSi_{2}Cr) .................................3
Crystal structure data of complex 12a (C_{27}H_{21}O_{6}PW): 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) Å³, Z = 4, ρ_cal = 1.736 Mg m⁻³, 2θ_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, wR_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_{6}PSi_{2}W): 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) Å³, Z = 2, ρ_cal = 1.647 Mg m⁻³, 2θ_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, wR_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) 1.622(2), P–H 1.38(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}, θ_{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}, θ_{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).