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Contrasting *cyclo*-P₃ Ligand Transfer Reactivity of Valence-Isoelectronic Aryloxide Complexes [(P₃)Nb(ODipp)₃]⁻ and [(P₃)W(ODipp)₃]



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Reduction of mer-Cl₃W(ODipp)₃ with Na/Hg in the presence of P₄ in toluene afforded the orange complex (η^3 -P₃)W-(ODipp)₃ (δ_{31p} = -156 ppm, 10% isolated yield). Unlike the valence-isoelectronic anion [(η^3 -P₃)Nb(ODipp)₃]⁻, treatment with AsCl₃ of the neutral (η^3 -P₃)W(ODipp)₃ did not transfer

the cyclo-P₃ ligand to generate AsP₃. Instead, this complex underwent aryloxide ligand transfer to form the red complex $(\eta^3$ -P₃)W(Cl)(ODipp)₂(THF) ($\delta_{^{31}P} = -143$ ppm, 32 % isolated yield).

Introduction

Lately, the activation of white phosphorus has received renewed interest from the research community in an effort to develop green chemistry routes to value-added phosphorus-containing chemicals.^[1] Although the maturing field of coordination chemistry of P₄ has begun to uncover pathways towards efficient access to such chemicals, examples are still relatively rare.^[1] A common route for functionalizing P₄ has been to form *cyclo*-P₃ complexes, as such compounds have been structurally characterized for most metals in groups 5–10 (except group 7) and thorium.^[2–12] However, other than the formation of multinuclear P₃ complexes, the functionalization of *cyclo*-P₃ ligands has only been reported for very few cases, such as in the formation of η^3 -RP₃ triphosphirene ligands^[4,13] or P₆ fragments.^[5]

The $[(\eta^3-P_3)Nb(ODipp)_3]^-$ anion $([1-Nb]^-$, Dipp = 2,6*i*Pr₂C₆H₃) is the only complex that has been reported to yield products in which the P₃ fragment is completely removed from the transition metal center.^[2,6] Treatment with appropriate reagents allowed the transfer of the *cyclo*-P₃ unit to form either polycyclic Ph₃SnP₃(C₆H₈)^[6] or tetrahedral AsP₃.^[2] While the former can be further employed for a formal [P₃]^{3–} group transfer,^[6] the latter has been shown to exhibit a wide range of reactivity.^[2,14] As a result, we

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decided to expand the scope of reactions that might afford the AsP₃ molecule and became interested in investigating the dependence of AsP₃ formation in the absence of an anionic charge by using the valence-isoelectronic, neutral complex $(\eta^3-P_3)W(ODipp)_3$ (1-W).

cyclo-P₃ complexes have typically been synthesized by treatment of P₄ with precursors containing metals in low oxidation states^[7,8] or very labile ligands,^[9,10,15] but they have also been prepared from phosphorus-rich complexes (with P₄ ligands)^[16] or from terminal metal phosphides upon treatment with P2 sources.^[11,12] There have been, however, only three examples of structurally characterized η^3 -P3 complexes bearing aryloxide or alkoxide ligands.^[2,7,10] Neutral complex $(\eta^3 - P_3)W(OCH_2tBu)_3(HNMe_2)$ has been prepared by the treatment of $W_2(OCH_2tBu)_6(HNMe_2)_2$ with P₄ in 30% yield,^[7] while $(\eta^3 - P_3)Mo(OCy)_3(HN[iPr]Ar)$ (Cy = cyclohexyl, Ar = 3,5-Me₂C₆H₃) has been isolated in 41% yield by the treatment of $(\eta^3 - P_3)Mo(N[iPr]Ar)_3$ with cyclohexanol.^[10] Anionic complex [1-Nb]⁻ was synthesized in a single step by the reduction of Cl₂Nb(ODipp)₃ with Na/Hg in the presence of P₄ in 57% yield.^[2] Of these three complexes, only the reactivity of the niobium complex has been investigated.^[2,6] We report here the synthesis of neutral tungsten complex 1-W by reduction of complex Cl₃W- $(ODipp)_3$ in the presence of P₄, as well as the strikingly contrasting reactivity with AsCl₃ that we observe for the valence-isoelectronic complexes $[(P_3)M(ODipp)_3]^{n-}$ (M = Nb, n = 1; M = W, n = 0).

Results and Discussion

The published synthesis of $mer-Cl_3W(ODipp)_3$ by heating WCl₆ and HODipp at reflux involves tedious column chromatography to purify the desired product.^[17] We have

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been able to scale up this protocol and simplify the purification procedure by simply recrystallizing the product from hexane at -35 °C to afford a yield of 61% (16 g). Reduction of this *mer*-Cl₃W(ODipp)₃ complex with a mild reducing agent such as zinc powder stopped at the tungsten(V) complex. The paramagnetic, orange-red complex Cl₂W(ODipp)₃-(THF) could be recrystallized from diethyl ether at -35 °C in 82% yield and was observed to be isostructural to the precursor for the [**1-Nb**]⁻ anion,^[2] only differing in the Cl-M–Cl angles: 174.02(2)° for tungsten (Figure S1) and 162.41(4)° for niobium.

Since formation of $[1-Nb]^-$ had been found to proceed most efficiently when sodium amalgam was used as the reducing agent in the presence of P₄, the same conditions were tested with the *mer*-Cl₃W(ODipp)₃ precursor. However, a *cyclo*-P₃ product could not be obtained by means of a Na/Hg reduction in the presence of P₄ in THF. Only upon changing the solvent to toluene could the formation of the neutral **1-W** complex be observed. Stirring Cl₃W(ODipp)₃ in the presence of P₄ and excess Na/Hg (0.7%) led to the formation of an orange-red mixture within 10 min, consistent with the formation of a tungsten(V) species (Scheme 1). Continued stirring led to a black mixture within 30 min, but complete consumption of the tungsten(VI) precursor was only observed after 3.5 h (¹H NMR spectroscopy).



Scheme 1. Synthesis of $(\eta^3\mbox{-}P_3)W(\mbox{ODipp})_3$ (1-W) and reactivity with $AsCl_3.$

After repeated attempts, the isolated yield of **1-W** could only be optimized to 10%. This is likely due to an unselective reductive process. Indeed, a side-product consistent with this was identified as the previously reported complex $W(ODipp)_4$.^[18] Ligand exchange reactions for tungsten complexes with aryloxide or alkoxide ligands are well known,^[19] but for niobium complexes such behavior has been reported exclusively for homoleptic complexes.^[20] These observations seem to suggest a greater lability of the ODipp ligand under reducing conditions in the presence of alkali metal ions for tungsten as compared with niobium.

The ¹H NMR spectrum of **1-W** reveals a single aryloxide environment with a doublet-septuplet aliphatic pair and two aromatic multiplets. It exhibits a sharp ³¹P NMR signal at $\delta = -156$ ppm, with tungsten-183 satellites (¹J₁₈₃W³¹P = 9 Hz). These data are similar to those reported for (η^3 -P₃)-W(OCH₂*t*Bu)₃(HNMe₂) ($\delta = -205$ ppm, 16 Hz).^[7] X-ray-quality crystals of $(\eta^3-P_3)W(ODipp)_3$ were grown from a concentrated diethyl ether solution at -35 °C. The solid-state structure of **1-W** (Figure 1) is very similar to that of the previously reported anion [**1-Nb**]^{-,[2]} The W–P distances [2.4389(7)–2.4471(7) Å] are approximately 0.08 Å shorter than the Nb–P ones, corresponding to a decrease in the covalent radii of tungsten compared to those of niobium (1.37 Å vs. 1.47 Å^[21]). The P–P bonds in **1-W** [2.174(1)–2.180(1) Å] are also shorter by about 0.02 Å relative to those in [**1-Nb**]⁻. Complex **1-W** exhibits shorter W– P distances (ca. 0.05 Å) and longer P–P distances (ca. 0.022 Å) relative to tungsten complex (η^3 -P₃)W(OCH₂*t*Bu)₃-(HNMe₂).^[7]



Figure 1. Solid-state structure (left) and ³¹P NMR signal (right, ${}^{1}J^{183}{}_{W}{}^{31}{}_{P} = 9$ Hz) of $(\eta^{3}{}-P_{3})W(ODipp)_{3}$ (1-W). Thermal ellipsoids are shown at the 50% probability level, and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–P2 2.1742(10), P1–P3 2.1804(10), P2–P3 2.1789(10), W1–P1 2.4471(7), W1–P2 2.4460(7), W1–P3 2.4389(7); P1–P2–P3 60.12(3), P2–P1–P3 60.05(3), P2–P3–P1 59.84(3), P1–W1–P2 52.76(2), P1–W1–P3 53.01(2), P2–W1–P3 52.98(2), P1–P2–W1 63.64(3).

Treatment of 1-W with either PCl₃ or AsCl₃ in THF led to very slow reactivity and no observable EP₃ formation (E = P, As). These observations stand in stark contrast to those obtained under similar conditions with [1-Nb], where complete conversion to AsP₃ was observed within 30 min after the addition of one equivalent of AsCl₃.^[2] Reaction of 1-W with either PCl₃ or AsCl₃ led to the same new metal complex. The reaction of 1-W with AsCl₃ was observed to be qualitatively faster than that with PCl₃. However, in the presence of one equivalent of AsCl₃ only a very small amount of 1-W was converted to this new product after 45 min. A small amount of 1-W was still present after 26 h of stirring in the presence of 2.6 equiv. of AsCl₃ in THF. The new metal-containing product was identified as $(\eta^3 -$ P₃)W(Cl)(ODipp)₂(THF) by X-ray diffraction (Figure 2). It could be isolated as red crystals in 32% yield by cooling a concentrated diethyl ether solution at -35 °C. In the solid state, the W-P distances [2.4801(10)-2.4888(10) Å] are elongated by about 0.04 Å with respect to those found in 1-W, probably a result of the higher coordination number around the tungsten atom. This, in turn, leads to a slight contraction in the P–P distances [2.1460(15)–2.1540(15) Å] by



about 0.03 Å. The ³¹P NMR spectrum of $(\eta^3-P_3)W(Cl)$ -(ODipp)₂(THF) has only one broad resonance at –143 ppm ($\Delta v_{1/2} = 413$ Hz), which can be explained by the low symmetry of the complex.



Figure 2. Solid-state structure of $(\eta^3-P_3)W(Cl)(ODipp)_2(THF)$ with thermal ellipsoids at the 50% probability level and hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–P2 2.1460(15), P1–P3 2.1519(14), P2–P3 2.1540(15), W1–P3 2.4801(10), W1–P1 2.4818(10), W1–P2 2.4888(10); P2–P1–P3 60.16(5), P1–P2–P3 60.06(5), P1–P3–P2 59.78(5), P3–W1–P1 51.40(3), P3–W1–P2 51.38(3), P1–W1–P2 51.16(4).

It is likely that, for the [1-Nb]⁻ anion, fast reactivity with group 15 element halides was favored by salt metathesis – as was shown to be the case when treatment with Ph₃SnCl yielded dinuclear complex Ph₃Sn($\eta^{1:2}$ -P₃)Nb(ODipp)₃.^[6] In contrast, neutral complex 1-W does not provide for such a thermodynamic sink and a fast initial step. This result is consistent with other aryloxide or alkoxide ligand exchange reactions observed upon treatment of neutral transition metal complexes with main-group halides.^[22]

Conclusions

The present work was motivated by a desire to understand the factors that enable efficient transfer of a cyclo-P₃ ligand to main-group acceptors when using the negatively charged complex [1-Nb]⁻. The present study of the valenceisoelectronic neutral complex 1-W containing niobium's diagonal relative element, tungsten, gave only evidence for halide/aryloxide ligand exchange upon treatment with ECl₃ (E = P, As), tempting us to speculate that the possibility for salt elimination (i.e., formation of a NaCl precipitate) together with the negative charge in the niobium system may make the cyclo-P₃ ligand respectively faster-reacting and more nucleophilic in the niobium system. Alternatively, the bonding in the MP₃ tetrahedron may be more covalent for tungsten (or molybdenum) than for niobium, thus enabling ancillary ligand exchange reactions to occur without disturbing the MP₃ unit. Studies of *neutral* niobium cyclo-P₃ complexes would be an interesting undertaking to further unravel the requirements for successful P₃-ligand functionalization and transfer reactivity.

Experimental Section

Methods: All manipulations were performed under a dry N₂ atmosphere, inside a glovebox, or by using a Schlenk line. Solvents were obtained anhydrous and oxygen-free. [D₆]Benzene was acquired from Cambridge Isotope Laboratories, dried with Na/benzophenone, and distilled prior to use. White phosphorus was acquired from ThermPhos International. NMR spectra were obtained with Varian Mercury 300 or Bruker Avance-400 instruments equipped with SpectroSpin or Magnex Scientific superconducting magnets, and the signals were referenced to appropriate solvent resonances.^{[23] 31}P NMR spectra were referenced externally against 85% H₃PO₄ ($\delta^{31}_{P} = 0$ ppm).

 $(\eta^{3}-P_{3})W(ODipp)_{3}$ (1-W): A sample of Na (0.168 g, 7.31 mmol, 6 equiv.) was added to a sample of Hg (24 g) and the 0.7% amalgam was cooled to room temperature. A P4 (0.182 g, 1.47 mmol, 1.2 equiv.) and mer-Cl₃W(ODipp)₃ (1.006 g, 1.22 mmol, 1 equiv.) solution in toluene (90 mL) was added to the Na amalgam, and the mixture was stirred vigorously at room temperature for 3.5 h. This was then filtered through a plug of Celite, and the residues were washed with toluene (3×20 mL). Volatiles from the red filtrate were removed under reduced pressure, and the orange residue was dissolved in pentane (50 mL), filtered, and dried to yield the crude product (181 mg). This was redissolved in pentane (20 mL), and the solution was stored at -35 °C overnight. The resulting orange crystalline solid was collected on a fritted glass filter, washed with thawing pentane (20 mL), and dried to yield analytically pure 1-W (96 mg, 0.12 mmol, 10% yield). X-ray quality crystals were grown at -35 °C from a concentrated diethyl ether solution. ¹H NMR (300 MHz, [D₆]benzene, 20 °C): δ = 7.13 (m, 6 H), 7.00 (m, 3 H), 3.42 (sept, ${}^{3}J_{HH} = 6.8$ Hz, 6 H), 1.26 (d, ${}^{3}J_{HH} =$ 6.8 Hz, 36 H) ppm. ¹³C NMR (101 MHz, $[D_6]$ benzene, 20 °C): δ = 157.7, 139.7, 125.9, 124.0, 27.4, 24.5 ppm. ³¹P NMR (121 MHz, [D₆]benzene, 20 °C): $\delta = -156.4 (\Delta v_{1/2} = 2.1 \text{ Hz}; {}^{1}J_{183}W^{31}P = 9 \text{ Hz})$ ppm. C₃₆H₅₁O₃P₃W (808.55): calcd. C 53.48, H 6.36; found C 53.06. H 6.15.

 $(\eta^3-P_3)W(Cl)(ODipp)_2(THF)$: Caution: AsCl₃ is highly toxic and should be handled with the utmost care! AsCl₃ (35 mg, 0.19 mmol, 2.6 equiv.) from a THF stock solution was diluted in THF (3 mL), while 1-W (60 mg, 0.07 mmol, 1 equiv.) was dissolved in THF (2 mL). The just-thawed AsCl₃ solution was added to the thawing 1-W solution. The reaction mixture was warmed up to room temperature and stirred for 26 h, after which all volatiles were removed under reduced pressure. The resulting residue was redissolved in pentane (8 mL) and then stored at -35 °C. The red crystalline solids were collected on a fritted glass filter and washed with thawing pentane (1 mL) to yield analytically pure (n³-P₃)W(Cl)(ODipp)₂-(THF) (18 mg, 0.024 mmol, 32% yield). X-ray quality crystals were grown out of a concentrated diethyl ether solution at -35 °C. ¹H NMR (400 MHz, [D₆]benzene, 20 °C): δ = 7.23 (d, ³J_{HH} = 7.7 Hz, 4 H), 7.05 (t, ${}^{3}J_{HH} = 7.7$ Hz, 2 H), 4.10 (m, 4 H), 3.35 (sept, ${}^{3}J_{HH}$ = 6.8 Hz, 4 H), 1.35 (m, 16 H), 1.28 (d, ${}^{3}J_{HH}$ = 6.8 Hz, 12 H) ppm. ¹³C NMR (101 MHz, [D₆]benzene, 20 °C): δ = 159.0, 137.7, 125.9, 123.9, 71.2, 27.5, 25.5, 24.5, 23.8, 22.7 ppm. ³¹P NMR (162 MHz, [D₆]benzene, 20 °C): δ = -142.7 ($\Delta v_{1/2}$ = 413 Hz) ppm. C₂₈H₄₂ClO₃P₃W (738.85): calcd. C 45.52, H 5.73; found C 45.33, H 5.69.

X-ray Crystal Structure Analysis: Crystals were mounted in hydrocarbon oil on a nylon loop and diffraction data were collected at 100 K on a Siemens platform three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromatized Mo- K_a radiation ($\lambda = 0.71073$ Å) performing ϕ and ω scans. General refinement details are discussed elsewhere.^[24] **Crystal Data for Cl₂W(ODipp)₃(THF):** C₄₀H₅₉Cl₂O₄W, monoclinic, $P2_1/n$ space group, a = 10.4827(6) Å, b = 23.1828(14) Å, c = 16.5126(10) Å, $\beta = 95.8970(10)^\circ$, V = 3991.6(4) Å³, Z = 4, $\rho_{calcd.} = 1.429$ gcm⁻³, $\mu = 3.065$ mm⁻¹. A total of 88816 reflections were collected in the 2θ range of $1.52-29.57^\circ$, 11194 being unique ($R_{int} = 0.0541$). An analytical absorption correction was applied on the basis of the intensities of equivalent reflections ($T_{min} = 0.5628$, $T_{max} = 0.7461$). Least-squares refinement on 436 parameters converged normally with R_1 [$I > 2\sigma(I)$] = 0.0248, $wR_2 = 0.0587$, GOOF = 1.062.

Crystal Data for $(\eta^3-P_3)W(\text{ODipp})_3$: $C_{36}H_{51}O_3P_3W$, monoclinic, $P2_1/n$ space group, a = 10.6955(9) Å, b = 17.2654(14) Å, c = 20.4942(16) Å, $\beta = 103.4440(10)^\circ$, V = 3680.8(5) Å³, Z = 4, $\rho_{calcd.} = 1.459$ g cm⁻³, $\mu = 3.301$ mm⁻¹. A total of 84532 reflections were collected in the 2θ range of 2.31–27.47°, 8453 being unique ($R_{int} = 0.0530$). An analytical absorption correction was applied on the basis of the intensities of equivalent reflections ($T_{min} = 0.5728$, $T_{max} = 0.8018$). Least-squares refinement on 400 parameters converged normally with R_1 [$I > 2\sigma(I)$] = 0.0219, $wR_2 = 0.0532$, GOOF = 1.076.

Crystal $(\eta^3-P_3)W(Cl)(ODipp)_2(THF)\cdot\frac{1}{2}THF:$ Data for $C_{30}H_{46}ClO_{3.5}P_3W$, triclinic, \bar{P} space group, a = 9.6030(11) Å, b =13.6166(16) Å, c = 14.0563(16) Å, $a = 110.625(2)^{\circ}$, $\beta = 103.335(2)^{\circ}$, $\gamma = 91.693(2)^{\circ}, V = 1661.4(3) \text{ Å}^3, Z = 2, \rho_{\text{calcd.}} = 1.549 \text{ gcm}^{-3}, \mu = 1.549 \text{ gcm}^{-3}$ 3.731 mm⁻¹. A total of 36833 reflections were collected in the 2θ range of 1.60–29.57°, 9231 being unique ($R_{int} = 0.0449$). An analytical absorption correction was applied on the basis of the intensities of equivalent reflections ($T_{\min} = 0.5519$, $T_{\max} = 0.7461$). Leastsquares refinement on 424 parameters converged normally with R_1 $[I > 2\sigma(I)] = 0.0362, wR_2 = 0.0985, \text{ GOOF} = 1.075.$ The bound THF was disordered over two positions with occupancies refined freely, and their sum was restrained to unity. The free THF was disordered over two symmetry-related positions with occupancies restrained to 1/2.

CCDC-954448 [for Cl₂W(ODipp)₃(THF)], -954449 [for (η^3 -P₃)-W(ODipp)₃], and -954450 [for (η^3 -P₃)W(Cl)(ODipp)₂(THF)· ½THF] 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.

Supporting Information (see footnote on the first page of this article): Solid-state structure of $Cl_2W(ODipp)_3(THF)$, optimized protocols for *mer*- $Cl_3W(ODipp)_3$ and $Cl_2W(ODipp)_3(THF)$, and complete NMR spectroscopic details for all compounds.

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- a) M. Caporali, L. Gonsalvi, A. Rossin, M. Peruzzini, *Chem. Rev.* 2010, *110*, 4178–4235; b) B. M. Cossairt, N. A. Piro, C. C. Cummins, *Chem. Rev.* 2010, *110*, 4164–4177; c) M. Scheer, G. Balázs, A. Seitz, *Chem. Rev.* 2010, *110*, 4236–4256; d) C. D. Martin, C. M. Weinstein, C. E. Moore, A. L. Rheingoldb, G. Bertrand, *Chem. Commun.* 2013, *49*, 4486–4488.
- [2] B. M. Cossairt, M.-C. Diawara, C. C. Cummins, Science 2009, 323, 602.

- [3] a) E. B. Hulley, P. T. Wolczanski, E. B. Lobkovsky, Chem. Commun. 2009, 6412–6414; b) B. L. Tran, M. Singhal, H. Park, O. P. Lam, M. Pink, J. Krzystek, A. Ozarowski, J. Telser, K. Meyer, D. J. Mindiola, Angew. Chem. 2010, 122, 10067; Angew. Chem. Int. Ed. 2010, 49, 9871-9875; c) H. A. Spinney, N. A. Piro, C. C. Cummins, J. Am. Chem. Soc. 2009, 131, 16233-16243; d) S. Welsch, M. Bodensteiner, M. Dusek, M. Sierka, M. Scheer, Chem. Eur. J. 2010, 16, 13041-13045; e) L. Yoong Goh, C. K. Chu, R. C. S. Wong, J. Chem. Soc., Dalton Trans. 1989, 1951-1956; f) R. Ahlrichs, D. Fenske, K. Fromm, H. Krautscheid, U. Krautscheid, O. Treutler, Chem. Eur. J. 1996, 2, 238-244; g) P. Barbaro, M. Di Vaira, M. Peruzzini, S. Seniori Constantini, P. Stoppioni, Eur. J. Inorg. Chem. 2005, 1360-1368; h) C. Bianchini, M. Di Vaira, A. Meli, L. Sacconi, Inorg. Chem. 1981, 20, 1169-1173; i) C. Bianchini, M. Di Vaira, A. Meli, L. Sacconi, J. Am. Chem. Soc. 1981, 103, 1448-1452; j) M. Di Vaira, M. P. Ehses, M. Peruzzini, P. Stoppioni, Polyhedron 1999, 18, 2331-2336; k) M. Di Vaira, M. P. Ehses, P. Stoppioni, Inorg. Chem. 2000, 39, 2199-2205; 1) M. Di Vaira, C. A. Ghilardi, S. Midollini, L. Sacconi, J. Am. Chem. Soc. 1978, 100, 2550-2551; m) M. Di Vaira, D. Rovai, P. Stoppioni, Polyhedron 1990, 9, 2477-2481; n) M. Di Vaira, P. Stoppioni, M. Peruzzini, J. Chem. Soc., Dalton Trans. 1990, 109-113; o) P. Dapporto, L. Sacconi, P. Stoppioni, F. Zanobini, Inorg. Chem. 1981, 20, 3834–3839; p) O. J. Scherer, B. Werner, G. Heckmann, G. Wolmershauser, Angew. Chem. 1991, 103, 562; Angew. Chem. Int. Ed. Engl. 1991, 30, 553-555.
- [4] M. Di Vaira, P. Stoppioni, S. Midollini, F. Laschi, P. Zanello, Polyhedron 1991, 10, 2123–2129.
- [5] a) M. Di Vaira, P. Stoppioni, *Polyhedron* 1994, 13, 3045–3051;
 b) E. B. Hulley, P. T. Wolczanski, E. B. Lobkovsky, *Chem. Commun.* 2009, 42, 6412–6414.
- [6] B. M. Cossairt, C. C. Cummins, Angew. Chem. 2010, 122, 1639; Angew. Chem. Int. Ed. 2010, 49, 1595–1598.
- [7] M. H. Chisholm, J. C. Huffman, J. W. Pasterczyk, *Inorg. Chim. Acta* 1987, 133, 17–18.
- [8] M. Di Vaira, L. Sacconi, P. Stoppioni, J. Organomet. Chem. 1983, 250, 183–195.
- [9] M. Scheer, G. Friedrich, K. Schuster, Angew. Chem. 1993, 105, 641–643; Angew. Chem. Int. Ed. Engl. 1993, 32, 593–594.
- [10] F. H. Stephens, M. J. A. Johnson, C. C. Cummins, O. P. Kryatova, S. V. Kryatov, E. V. Rybak-Akimova, J. E. McDonough, C. D. Hoff, J. Am. Chem. Soc. 2005, 127, 15191–15200.
- [11] N. A. Piro, C. C. Cummins, J. Am. Chem. Soc. 2008, 130, 9524– 9535.
- [12] D. Tofan, B. M. Cossairt, C. C. Cummins, *Inorg. Chem.* 2011, 50, 12349–12358.
- [13] a) A. Barth, G. Huttner, M. Fritz, L. Zsolnai, Angew. Chem.
 1990, 102, 956–958; Angew. Chem. Int. Ed. Engl. 1990, 29, 929–931; b) S. Beyreuther, J. Hunger, G. Huttner, S. Mann, L. Zsolnai, Chem. Ber. 1996, 129, 745–757; c) G. Capozzi, L. Chiti, M. Di Vaira, M. Peruzzini, P. Stoppioni, J. Chem. Soc., Chem. Commun. 1986, 1799–1800.
- [14] a) B. M. Cossairt, C. C. Cummins, J. Am. Chem. Soc. 2009, 131, 15501–15511; b) B. M. Cossairt, C. C. Cummins, Chem. Eur. J. 2010, 16, 12603–12608.
- [15] a) C. Bianchini, C. Mealli, A. Meli, L. Sacconi, *Inorg. Chim. Acta* 1979, 37, L543–L544; b) C. A. Ghilardi, S. Midollini, A. Orlandini, L. Sacconi, *Inorg. Chem.* 1980, 19, 301–306; c) T. Gröer, M. Scheer, *Z. Anorg. Allg. Chem.* 2000, 626, 1211–1216; d) O. J. Scherer, T. Dave, J. Braun, G. Wolmershäuser, *J. Organomet. Chem.* 1988, 350, C20–C24.
- [16] a) M. Scheer, S. Deng, O. J. Scherer, M. Sierka, Angew. Chem.
 2005, 117, 3821; Angew. Chem. Int. Ed. 2005, 44, 3755–3758;
 b) M. Peruzzini, J. A. Ramirez, F. Vizza, Angew. Chem. 1998, 110, 2376; Angew. Chem. Int. Ed. 1998, 37, 2255–2257.
- [17] F. Quignard, M. Leconte, J. M. Basset, L. Y. Hsu, J. J. Alexander, S. G. Shore, *Inorg. Chem.* **1987**, *26*, 4272–4277.
- [18] M. L. Listemann, R. R. Schrock, J. C. Dewan, R. M. Kolodziej, *Inorg. Chem.* **1988**, 27, 264–271.



- [19] a) A. Lehtonen, R. Sillanpää, *Polyhedron* 2000, 19, 2579–2584;
 b) A. Lehtonen, R. Sillanpää, *Inorg. Chem.* 2001, 40, 6047–6051;
 c) A. Lehtonen, R. Sillanpää, *Polyhedron* 2002, 21, 1017–1022;
 d) A. Lehtonen, R. Sillanpää, *Polyhedron* 2003, 22, 2755–2760;
 e) M. R. Churchill, Y.-J. Li, K. H. Theopold, R. R. Schrock, *Inorg. Chem.* 1984, 23, 4472–4476.
- [20] a) S. Lim, J. C. Lee, D. S. Sohn, W. I. Lee, I.-M. Lee, *Chem. Mater.* 2002, 14, 1548–1554; b) M. K. Sharma, A. Singh, R. C. Mehrotra, *Transition Met. Chem.* 2002, 27, 115–119.
- [21] P. Pyykkö, M. Atsumi, Chem. Eur. J. 2009, 15, 186–197.
- [22] a) V. Cadierno, M. Zablocka, B. Donnadieu, A. Igau, J.-P. Majoral, A. Skowronska, *Chem. Eur. J.* 2001, *7*, 221–229; b) A. Fischbach, F. Perdih, E. Herdtweck, R. Anwander, *Organometallics* 2006, *25*, 1626–1642; c) J. J. Doney, R. G. Bergman, C. H. Heathcock, *J. Am. Chem. Soc.* 1985, *107*, 3724–3726; d) N. Steiner, E. Ehrenstorfer, J. Chen, W. Beck, *Chem. Ber.* 1988,

121, 275–279; e) D. J. Krysan, P. B. Mackenzie, J. Am. Chem. Soc. 1988, 110, 6273–6274; f) S. Roelens, J. Chem. Soc. Perkin Trans. 2 1988, 2105–2110; g) H. Yasuda, H. Yamamoto, K. Yokota, A. Nakamura, Chem. Lett. 1989, 7, 1309–1312; h) J. Christoffers, R. G. Bergman, Angew. Chem. 1995, 107, 2423; Angew. Chem. Int. Ed. Engl. 1995, 34, 2266–2267; i) T. Braun, S. Rothfeld, V. Schorlemer, A. Stammler, H.-G. Stammler, Inorg. Chem. Commun. 2003, 6, 752–755; j) S. Ogoshi, K. Tonomori, M. Oka, H. Kurosawa, J. Am. Chem. Soc. 2006, 128, 7077–7086.

- [23] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* 2010, 29, 2176–2179.
- [24] D. Tofan, C. C. Cummins, *Chem. Sci.* 2012, 3, 2474–2478. Received: September 3, 2013 Published Online: October 30, 2013

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