the chemical equivalence of the phosphorus atoms. The crystal structure of 1 was determined by X-ray diffraction.[10] A drawing with the main bond distances and angles is shown in Figure 1.

The cationic complex consists of an isosceles triangle "cluster" of copper atoms (Cu–Cu distances 2.594 (3) Å (average)) with a dppm ligand bridging each edge to form a roughly planar $[Cu_3P_6]^+$ core (the deviations of the P atoms from the Cu3 plane are as follows: P1, 0.051 (5); P2, 0.683 (5); P3, -0.747 (5); P4, -0.776 (5); P5, 0.497 (5); P6, 0.562 (5) Å). The most remarkable feature is the presence of two triply bridging phenylacetylide groups, forming an unprecedented bicapped trigonal organocopper(I) derivative. The bridging mode of the alkynyl groups is highly asymmetric, as illustrated by the different bond lengths of Cu–C (2.063 (18)–2.342 (17) Å) or bond angles between the alkynyl groups and each copper atom (125.9 (15)–145.8 (18)°; see Figure 1). The intersection angle between the two bonding lines of the phenylacetylide groups, C(4)–C(5)–C(6) and C(12)–C(13)–C(14), is 166.6 (14)°. The linearity of each phenylacetylide group (bond angles of 177.3 (23) and 178.4 (21)°) and the C≡C distances (1.214 (24) and 1.209 (24) Å) are consistent with typical metal–acetylide σ bonding, and hence, the complex shows a five-center–four-electron bonding system, a very uncommon case in organocopper chemistry.

Another relevant feature concerning the Cu–Cu and Cu–C distances should be mentioned. Although the copper–copper distances (2.594 (3) Å (average)) are consistent with nonbonding interactions,[11] they are shorter than those found in **2** (cf. 2.997 (3) Å (average)).[8a] In contrast, the Cu_3–C distances are significantly larger (2.211 (16) Å for C4 and 2.195 (19) Å for C12 (average); cf. **2**, 2.027 (14) Å (average)). This seems to suggest that the bonding combination between the copper orbitals and the two sp orbitals is more localized at the metallic system in the Cu_3C_2 core (type C) than in the analogous Cu_3C (type B). As expected, the Cu–Cu and Cu–C bond lengths are larger than those found[7b] in the case of the three-center–two-electron alkynyl-bridged μ_2-η^1 system (type A; Cu–C, 1.984 (7)–2.130 (6) Å; Cu–Cu, 2.474 (4) Å).

A solution of complex 1 in CH_2Cl_2 (containing traces of HCl) gives the mixed-bridge derivative $[Cu_3(\mu_3\text{-}Cl)(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)(\mu\text{-dppm})_3][BF_4]$ (**4**) with a triply bridging chlorine.[12] These peculiar bicapping phenylacetylide and phenylacetylide–chloride systems, found in **1** and **4**, respectively, are structurally and electronically related to similar *triangulo*-M_3 (dppm) clusters (M = Ni, Pd, Pt) with triply bridging carbonyl or methyl isocyanide ligands.[13,14] Therefore, the new Cu_3 complexes bridged by dppm ligands offer an unusual opportunity to compare structures and reactivity between formally metal d^{10} clusters, which may be of interest in elucidating the role of catalytic amounts of Pd(0) phosphine complexes in the copper(I)-mediated couplings of acetylenes.[15]

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Supplementary Material Available: Listings of positional parameters for non-hydrogen atoms, bond lengths and angles, anisotropic temperature factors, positional parameters of hydrogen atoms, and torsion angles (23 pages). Ordering information is given on any current masthead page.

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[10] Crystals of the complex were obtained by slow diffusion of Et_2O into a THF solution of 1. Crystal data for 1: $C_{91}H_{76}BCu_3F_4P_6$, M_r = 1632.9, monoclinic, space group $P2_1/c$, a = 14.613 (1) Å, b = 21.863 (1) Å, c = 26.672 (1) Å, β = 102.86 (1)°, V = 8307.4 (1) Å^3, Z = 4, ρ_{calcd} = 1.31 g/cm^3, T = 293 K; crystal dimensions 0.30 × 0.20 × 0.13 mm^3; Mo Kα radiation (λ = 0.71073 Å), graphite monochromated; 12486 reflections measured on an Enraf-Nonius CAD4 (ω–2θ scan technique), range $0 < \theta < 25°$ and $-16 \le h \le 15$, $0 \le k \le 23$, $0 \le l \le 29$; 11440 unique reflections (R_{int} = 0.042, averaging some double measured) and 4813 observed ($I > 3\sigma(I)$). Semiempirical and empirical absorption corrections were applied; μ = 9.28 cm^{-1}. The structure was solved by Patterson interpretation (SHELXS 86) and anisotropically refined (SHELX 76) to a final R = 0.077 (910 parameters and unit weights); maximum shift/error 0.28, p_{max} = 0.76 e/Å^3.

[11] Cotton, F. A.; Feng, X.; Matusz, M.; Bli, R. *J. Am. Chem. Soc.* **1988**, *110*, 7077 and references therein.

[12] Pale yellow solid, Δ_M(acetone) = 140 Ω^{-1} cm^2 mol^{-1}. IR (KBr): ν(B—F) = 1055 (s, br) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.15 (m, 6 H, CH_2P_2), 6.7–7.2 (m, 60 H, Ph_2P), 7.3–7.6 (m, 5 H, PhC≡C). $^{31}P\{^1H\}$ NMR: δ -8.98. Anal. Calcd for $C_{83}H_{71}BCu_3ClF_4P_6\cdot{}^1/_2CH_2Cl_2$: C, 62.12; H, 4.45. Found: C, 61.94; H, 4.63. The structure has been confirmed by an X-ray crystallographic determination: García-Granda, S.; Aguirre, A. Personal communication.

[13] Ferguson, G.; Lloyd, B. R.; Puddephatt, R. J. *Organometallics* **1986**, *5*, 344. Manojlovic-Muir, L. J.; Muir, K. W.; Lloyd, B. R.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1983**, 1336. Bradford, A. M.; Jennings, M. C.; Puddephatt, R. J. *Organometallics* **1988**, *7*, 792.

[14] Ratliff, K. S.; Broeker, G. K.; Fanwick, P. E.; Kubiak, C. P. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 395; *Angew. Chem.* **1990**, *102*, 405.

[15] Brandsma, L. *Preparative Acetylenic Chemistry*, 2nd ed.; Elsevier: Amsterdam, 1988; p 231.

Thermal and Photochemical Decarbonylation of $(MeC_5H_4)_2Nb(\eta^2\text{-}CO_2)CH_2SiMe_3$

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Summary: $(MeC_5H_4)_2Nb(\eta^2\text{-}CO_2)CH_2SiMe_3$ (**1**) undergoes thermolysis at 60 °C in THF to produce $(MeC_5H_4)_2Nb({=}O)CH_2SiMe_3$ (**2**). The structure of **2** has been confirmed by X-ray diffraction. The **1** → **2** conversion is promoted photochemically, occurring at -20 °C within minutes upon UV irradiation.

Despite expanding interest in transition-metal-mediated chemical[1] and electrochemical[2] transformations of carbon dioxide, the reactivity of *coordinated* CO_2 remains largely unexplored.[3] In this context we reported recently the first

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[1] Reviews: (a) Behr, A. *Carbon Dioxide Activation by Metal Complexes*; VCH: Weinheim, Germany, 1988. (b) Ito, T.; Yamamoto, A. In *Organic and Bioorganic Chemistry of Carbon Dioxide*; Inoue, S., Yamazaki, N., Eds.; Halstead Press: New York, 1982; Chapter 3, pp 79–151. (c) Darensbourg, D.; Kudaroski, R. A. *Adv. Organomet. Chem.* **1983**, *22*, 129.

[2] DuBois, D. L.; Miedaner, A. *J. Am. Chem. Soc.* **1987**, *109*, 113. Fisher, B.; Eisenberg, R. *Ibid.* **1980**, *102*, 7361. Tezuka, M.; Yajima, T.; Tsuchiya, A.; Matsumoto, Y.; Uchida, Y.; Hidai, M. *Ibid.* **1982**, *104*, 6834.

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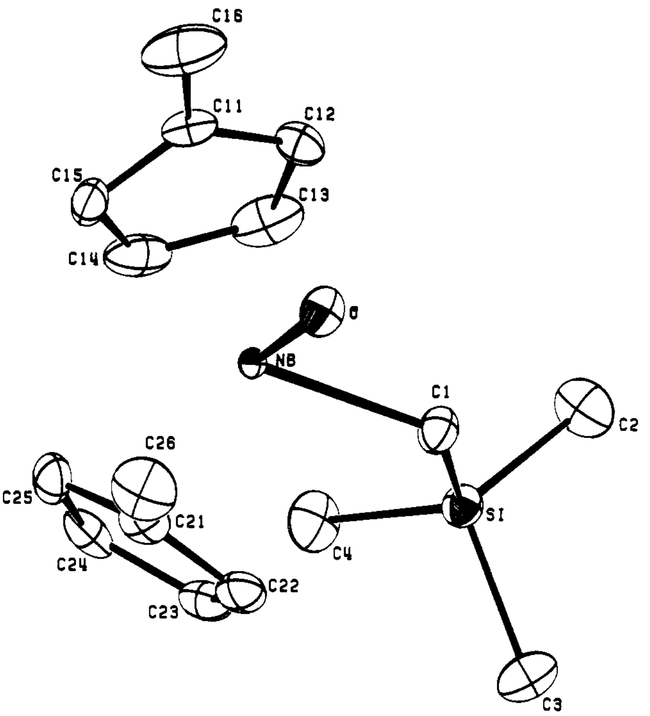
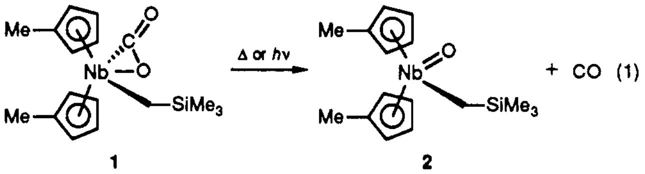


Figure 1. ORTEP diagram for 2. Thermal ellipsoids are shown at the 50% level. Selected bond lengths (Å) and angles (deg): Nb-O = 1.741 (3), Nb-C(1) = 2.246 (4), Nb-Cp(1) = 2.166 (4), Nb-Cp(2) = 2.183 (4); O-Nb-C(1) = 97.3 (1), Cp(1)-Nb-Cp(2) = 131.0 (1), Cp(1)-Nb-C(1) = 103.8, Cp(2)-Nb-C(1) = 104.1 (1), Nb-C(1)-Si = 129.5 (2).

example of *photoinduced* CO_2 disproportionation in the complex $Cp_2Mo(\eta^2\text{-}CO_2)$[4] and its dark reactions with electrophilic agents[5] and transition-metal hydrides.[6] With an eye toward modeling catalytically relevant insertion reactions of CO_2, we have initiated reactivity studies of $(MeC_5H_4)_2Nb(\eta^2\text{-}CO_2)CH_2SiMe_3$ (1),[7] the only well-characterized compound containing both coordinated CO_2 and alkyl ligands. Reported herein are our preliminary observations of the novel thermal and photochemical reactivity of 1, which features facile *decarbonylation* rather than *insertion* (*carboxylation*).

Although complex 1 is remarkably stable under ambient conditions, when heated at 60 °C in THF 1 disappears by a first-order process ($k \approx 4 \times 10^{-5}$ s^{-1}, monitored by NMR spectroscopy in THF-d_8) and is converted into the new substance 2, which could be isolated in pure form as a somewhat air-sensitive white solid (45% yield) after sublimation (60 °C/0.05 mm) of the reaction residue.[8] An uncharacterized insoluble material (polymer?) was also obtained whose MS exhibited prominent peaks corresponding to 1^+ and $(MeC_5H_4)_2NbO^+$. Complex 2 has no significant IR absorptions in the 1600–2000-cm^{-1} region, as expected for a carboxylate or metallo ester insertion product. Instead, a prominent peak at 837 cm^{-1}, a mass spectral maximum at *m/e* 354, and supporting ^1H and ^{13}C NMR spectra and elemental analysis[9] led us to identify 2 as the *oxo-alkyl* derivative $(MeC_5H_4)_2Nb(=O)CH_2SiMe_3$ formed by loss of CO from 1 (eq 1). This assignment was confirmed by single-crystal X-ray diffraction[10] (Figure 1). The structure of 2, one of a small number of crystallographically characterized oxo-alkyl complexes,[11] consists of a pseudotetrahedral Cp_2MXY arrangement with no unusual bond parameters.[12]



We have found that the transformation 1 → 2 is dramatically accelerated photochemically. When a colorless THF solution of 1 (λ_{max} 250 nm) at −20 °C is irradiated (450-W Hg lamp, through quartz), it is consumed in less than 30 min and oxo complex 2 can be isolated in good yield. Interestingly, we find that 2 is also photosensitive, since upon longer term irradiation (>2 h) the yield of 2 is drastically reduced with production of an insoluble Nb-containing material. With use of ferrioxalate actinometry the quantum yield for the 1 → 2 conversion was found to be relatively high, $\Phi \geq 0.17$.[13] That the oxo oxygen of 2 is derived substantially from the original CO_2 was demonstrated by isotopic labeling. Thus, irradiation of $(MeC_5H_4)_2Nb(\eta^2\text{-}C^{18}O_2)CH_2SiMe_3$ (ca. 25% enriched) produced 2 with significant incorporation of the label (ca. 5%[14]) as determined by MS.

Although formation of metal-oxo[15] and -oxide[16] complexes has been observed previously in reactions of CO_2

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[3] Aresta, M.; Quaranta, E.; Tommasi, I. *J. Chem. Soc., Chem. Commun.* **1988**, 450. Harlow, R. L.; Kinney, J. B.; Herskovitz, T. *J. Chem. Soc., Chem. Commun.* **1980**, 813. Forschner, T.; Menard, K.; Cutler, A. R. *J. Chem. Soc., Chem. Commun.* **1984**, 121. Giuseppetti, M. E.; Cutler, A. R. *Organometallics* **1987**, *6*, 970. Senn, D. R.; Gladysz, J. A.; Emerson, K.; Larsen, R. D. *Inorg. Chem.* **1987**, *26*, 2737.

[4] Belmore, K. A.; Vanderpool, R. A.; Tsai, J.-C.; Khan, M. A.; Nicholas, K. M. *J. Am. Chem. Soc.* **1988**, *110*, 2004.

[5] Tsai, J.-C.; Khan, M.; Nicholas, K. M. *Organometallics* **1989**, *8*, 2967.

[6] Tsai, J.-C.; Khan, M.; Nicholas, K. M. *Organometallics*, in press.

[7] Bristow, G. S.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1981**, 1145.

[8] The NMR spectrum of **2** before and after sublimation[9] was essentially unchanged.

[9] **2**: mp 70 °C; IR (KBr) 3087, 2958, 1507, 1250, 837, 705 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, δ) 5.92 (m, 2 H, Cp), 5.79 (m, 2 H, Cp), 5.69 (m, 2 H, Cp), 5.47 (m, 2 H, Cp), 2.04 (s, 6 H, Cp–CH_3), 0.70 (s, 2 H, CH_2Si), 0.06 (s, 9 H, $Si(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$, δ) 128.7, 114.5, 110.5, 109.9, 102.9, 31.0, 15.8, 3.5; MS (EI, 12 eV) *m/e* 354.2 (M^+), 339.0 ($M^+ - CH_3$), 267 ($M^+ - CH_2Si(CH_3)_3$). Anal. Calcd for $C_{16}H_{25}NbOSi$: C, 54.2; H, 7.1. Found: C, 53.6; H, 7.2.

[10] X-ray crystal data for **2**: crystals obtained from ethyl ether/hexane at −20 °C (data collected at −110 °C); $C_{16}H_{25}NbOSi$, fw = 354.37, space group $P2_12_12_1$; $a = 6.104$ (2) Å, $b = 11.564$ (3) Å, $c = 23.064$ (5) Å, $V = 1628.0$ Å^3, $Z = 4$, $D_c = 1.446$ g cm^{-3}, $F(000) = 712$, λ(Mo Kα) = 0.71069 Å, μ(Mo Kα) = 7.84 cm^{-1}. Cell dimensions and intensities of 2184 reflections ($2\theta_{max} = 55°$) were measured. The structure was solved by the heavy-atom method, and all non-hydrogen atoms were refined anisotropically. All calculations were carried out with the SHELX-76 program. For 1815 unique observed reflections ($I > 2\sigma(I)$) the final $R = 0.022$, $R_w = 0.022$, and GOF = 1.016. Full details of the structure determination are available as supplementary material.

[11] A recent compilation of oxometal X-ray structures lists only 15 oxometal-alkyl structures out of approximately 600 total: Nugent, W. A.; Mayer, J. M. In *Metal-Ligand Multiple Bonds*; Wiley: New York, 1988; pp 159–179.

[12] One other $Cp_2Nb(O)$(alkyl) complex has been crystallographically characterized: Mercier, R.; Douglade, J.; Amaudrut, J.; Sala-Pala, J.; Guerchais, J. E. *J. Organomet. Chem.* **1983**, *244*, 145. It is perhaps noteworthy that the Nb–C(1) distance (2.246 Å) is diminished significantly from that in the CO_2 complex (2.283 Å), whereas the Cp–Nb centroid distance increases (2.091 Å (av) to 2.174 Å (av)). We thank a reviewer for pointing out these effects.

[13] The lamp intensity was determined with use of ferrioxalate actinometry at the 260-nm Hg band (230–300-nm filter). Disappearance of **1** during irradiation was monitored by IR spectroscopy at 1735 cm^{-1} and the yield of **2** determined by isolation. The photodecomposition of **2** and losses obtained during isolation limit the quantum yield.

[14] Assuming no isotope effect, about 12% ^{18}O incorporation would be expected in **2** from labeled **1**. Some exchange with ^{16}O (from CO_2, H_2O, or O_2) may occur during irradiation and/or isolation.

[15] Bryan, J. C.; Geib, S. J.; Reingold, A. L.; Mayer, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 2326. Bryan, J. C.; Mayer, J. M. *Ibid.* **1990**, *112*, 2298. Alt, H. G.; Schwind, K. H.; Rausch, M. D. *J. Organomet. Chem.* **1987**, *321*, C9.

[16] Fachinetti, G.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1979**, *101*, 1767.

with metal complexes, the reactions of 1 described herein provide the first unequivocal examples of thermal and photochemical "CO_2 splitting" to M=O and CO of *coordinated CO_2*. This process parallels the scission of other η^2-unsaturated ligands such as RN=O[17] and RNC=O[18] bound to Cp_2Nb–X units. It is interesting to note, however, the contrasting photoinduced disproportionation (to CO and CO_3^{2-}) that is found for isoelectronic, structurally related $Cp_2Mo(\eta^2\text{-}CO_2)$[4] and for other complexes of the latter transition metals.[19] The partitioning between these two pathways appears to reflect the relative oxophilicity of early vs later transition metals. The nature of the electronic transition that gives rise to the conversion of 1 to oxo complex 2 is unclear at present, but involvement of a state (ground or excited) with character centered on the coordinated CO_2 seems imperative. Studies to address this question and to promote CO_2 insertions of 1 are underway.

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Supplementary Material Available: Tables of positional and thermal parameters and interatomic distances and angles for 2 (5 pages); a table of observed and calculated structure factors for 2 (8 pages). Ordering information is given on any current masthead page.

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[17] Middleton, A. R.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1980**, 1888.

[18] Antinolo, A.; Garcia-Liedo, S.; Martinez de Ilarduya, J.; Otero, A. *J. Organomet. Chem.* **1987**, *335*, 85.

[19] Maher, J. M.; Copper, N. J. *J. Am. Chem. Soc.* **1980**, *104*, 6796. Lee, G. R.; Maher, J. M.; Copper, N. J. *Ibid.* **1987**, *109*, 2956. References 1b and references therein.

Selective Metal to Carbon Bond Formation in the Synthesis of the First Rhenium Complexes with S_2CPCy_3 Ligands. X-ray Structures of $[MnRe(CO)_6(\mu\text{-}S_2CPCy_3)]$ and $[Re_2(CO)_8(\mu\text{-}S_2CPCy_3)]$

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Summary: Reactions of either $[Mn(CO)_3(S_2CPCy_3)(Br)]$ with $Na[Re(CO)_5]$ or $[Re(CO)_3(S_2CPCy_3)(Br)]$ with $Na[Mn(CO)_5]$ produce selectively the heterobimetallic complex $[MnRe(CO)_6(\mu\text{-}S_2CPCy_3)]$, which contains an unsymmetrical $\eta^2(S,S'),\eta^3(S,C,S')$-$S_2CPCy_3$ bridge donating eight electrons with the carbon atom of the S_2C group bonded to manganese; in contrast, the reaction of $[Re(CO)_3(S_2CPCy_3)(Br)]$ with $Na[Re(CO)_5]$ produces $[Re_2(CO)_8(\mu\text{-}S_2CPCy_3)]$, with a $\eta^1(S),\eta^1(S')$-S_2CPCy_3 bridge of four electrons and no carbon–rhenium bond. In apparent contradiction with previous theoretical predictions, all the experimental facts suggest a stronger ability for manganese, when compared to rhenium, to become attached to the carbon atom of the S_2CPCy_3 ligand.

The interest in complexes containing (trialkylphosphonio)dithiocarboxylato groups, S_2CPR_3, believed to be intermediates in carbon disulfide activation,[1] has produced a number of compounds in which the S_2CPR_3 adducts act as versatile ligands toward a very wide range of metals,[2,3] exhibiting a variety of coordination modes and, sometimes, new and unexpected structural types.[3,4b,c] In

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[1] See: Bianchini, C.; Mealli, C.; Meli, A.; Sabat, M. Transition Metal Complexes with Carbon Disulfide. Correlations between Stereochemistry and Reactivity. *Stereochemistry of Organometallic and Inorganic Compounds*; Elsevier: New York, 1986; Vol. 1, Chapter 3, p 196, and references therein.

[2] Yagupsky, M. P.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 2813. Clark, G. R.; Collins, T. J.; James, S. M.; Roper, W. R. *J. Chem. Soc., Chem. Commun.* **1976**, 475. Boniface, S. M.; Clark, G. R. *J. Organomet. Chem.* **1980**, *188*, 263. Usón, R.; Forniés, J.; Navarro, R.; Usón, M. A.; García, M. P.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1984**, 345. Usón, R.; Forniés, J.; Usón, M. A.; Yague, J. F.; Jones, P. G.; Meyer-Base, K. *J. Chem. Soc., Dalton Trans.* **1986**, 947. Usón, R.; Laguna, A.; Laguna, M.; Jones, P. G.; Fittschen, C. *J. Chem. Soc.., Dalton Trans.* **1987**, 3017. Werner, H.; Bertleff, W. *Chem. Ber.* **1980**, *113*, 267. Baker, P. K.; Broadley, K.; Connelly, N. G. *J. Chem. Soc., Dalton Trans.* **1982**, 471. Schenk, W. A.; Schwietzke, T.; Muller, H. *J. Organomet. Chem.* **1982**, *232*, C41. Gaffney, J. R.; Ibers, J. A. *Inorg. Chem.* **1982**, *21*, 2062. Armit, P. W.; Sime, W. J.; Stephenson, T. A.; Scott, L. *J. Organomet. Chem.* **1978**, *161*, 391. Baird, D. M.; Fanwick, P. E.; Barwick, T. *Inorg. Chem.* **1985**, *24*, 3753. Bianchini, C.; Innocenti, P.; Meli, A.; Orlandini, A.; Scapacci, G. *J. Organomet. Chem.* **1982**, *233*, 233. Bianchini, C.; Meli, A.; Orlandini, A. *Inorg. Chem.* **1982**, *21*, 4161. Bianchini, C.; Ghilardi, C. A.; Meli, A.; Orlandini, A.; Scapacci, G. *J. Chem. Soc., Dalton Trans.* **1983**, 1969. Bianchini, C.; Ghilardi, C. A.; Meli, A.; Orlandini, A. *Inorg. Chem.* **1983**, *22*, 2188. Bianchini, C.; Meli, A.; Dapporto, P.; Tofanari, A.; Zanello, P. *Inorg. Chem.* **1987**, *26*, 3677.

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