Organometallics 1987, 6, 110–114

Transition-Metal-Substituted Diphosphenes. 3.[1] Synthesis of Stable Diphosphenes with Iron and Ruthenium Substituents. X-ray Structure Analysis of $(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2\text{FeP}{=}\text{PC}_6\text{H}_2\text{-}t\text{-Bu}_3\text{-2,4,6}$

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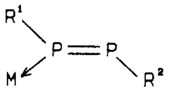
Received June 9, 1986

The reaction of $[(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2\text{MP(SiMe}_3)_2$ (M = Fe, Ru, Os) with 2,4,6-t-$\text{Bu}_3\text{C}_6\text{H}_2\text{PCl}_2$ (ArPCl_2) in THF at 20 °C afforded the novel diphosphenyl complexes (E)-$(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2\text{MP}{=}\text{PAr}$. Only the iron and ruthenium derivatives could be isolated from the reaction mixture as ocher-yellow or orange-yellow solids. The corresponding osmium derivative was trapped as its Ni(CO)_3 complex. Similarly stable $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{PPh}_3)\text{FeP}{=}\text{PAr}$ was generated from $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{PPh}_3)\text{FeP(SiMe}_3)_2$ and ArPCl_2. The novel coordination compounds were characterized by elemental analyses and spectroscopic methods (IR, ^{1}H, ^{13}C, and ^{31}P NMR, and mass spectroscopy). The molecular structure of $(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2\text{FeP}{=}\text{PAr}$ was established by a complete single-crystal diffraction study [$P2_1/c$ space group; $Z = 4$; $a = 12.414$ (6), $b = 15.582$ (7), $c = 20.347$ (8) Å; $\beta = 126.45$ (3)°].

The chemistry of two-coordinate, acyclic P^{III} compounds containing the P=P double bond, the diphosphenes, is of considerable current interest.[2] Diphosphenes and their higher congeners are versatile ligands in transition metal complexes and up to now can be encountered in at least seven different modes of coordination (A–G).[2,3]



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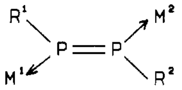

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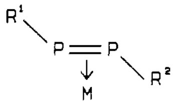

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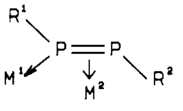

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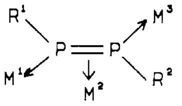

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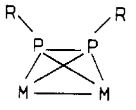

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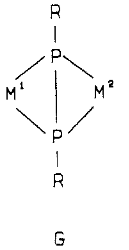

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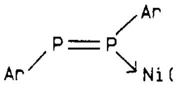
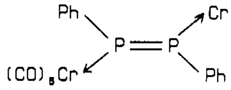


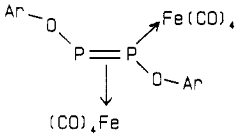
1



2

Ar=2,4,6-tri-t-butylphenyl

Compounds 1[4] and 2[5] are representative examples where only the phosphorus lone pairs of the P=P moiety are involved in complexation (types A and B). The η^2-coordination (type C) is known for several molybdenum,[6a] palladium, platinum,[7] and nickel complexes.[8] A combination of both modes of coordination is realized in compounds 3[9] and 4[5] (types D and E). Diphosphenes can also serve as building blocks in transition-metal clusters as represented by examples 5[10] and 6.[11] A diphosphene is encorporated in the butterfly arrangement of complex 7.[12]



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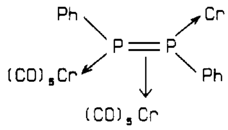

4

On the other hand, diphosphenes that are substituted by transition metals (as in I and II) instead of organic groups should be substantially different in character. In

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[1] Part 2: Weber, L.; Reizig, K.; Boese, R. *Angew. Chem.* **1986**, *98*, 737; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 755.

[2] Cowley, A. H. *Polyhedron* **1984**, *3*, 389 and references cited therein.

[3] Scherer, O. J. *Angew. Chem.* **1985**, *97*, 905; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 924 and references cited therein.

[4] Cowley, A. H.; Kilduff, J. E.; Lasch, J. G.; Norman, N. C.; Pakulski, M.; Wright, T. C. *Organometallics* **1984**, *3*, 1044.

[5] (a) Borm, J.; Zsolnai, L.; Huttner, G. *Angew. Chem.* **1983**, *95*, 1018; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 977; *Angew. Chem. Suppl.* **1983**, 1477. (b) Borm, J.; Huttner, G.; Orama, O.; Zsolnai, L. *J. Organomet. Chem.* **1985**, *282*, 53.

[6] Camillo, E.; Coda, A.; Prout, K.; Daran, J.-C. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1977**, *B33*, 2608.

[7] (a) Chatt, J.; Hitchcock, P. B.; Pidcock, A.; Warrens, C. P.; Dixon, K. R. *J. Chem. Soc., Chem. Commun.* **1982**, 932; *J. Chem. Soc., Dalton Trans.* **1984**, 2237. (b) Elmes, P. S.; Scudder, M. L.; West, B. O. *J. Organomet. Chem.* **1976**, *122*, 281.

[8] (a) Schäfer, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1979**, *B34*, 1358. (b) Fenske, D.; Merzweiler, K. *Angew. Chem.* **1984**, *96*, 600; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 635. (c) Schäfer, H.; Binder, D.; Fenske, D. *Angew. Chem.* **1985**, *97*, 522; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 523. (d) Jones, R. A.; Seeberger, M. H.; Whittlesey, J. *J. Am. Chem. Soc.* **1985**, *107*, 6424.

[9] Flynn, K. M.; Hope, H.; Murray, B. D.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1983**, *105*, 7750.

[10] (a) Vahrenkamp, H.; Wolters, D. *Angew. Chem.* **1983**, *95*, 152; *Angew. Chem., Int. Ed. Engl.* **1983**, *23*, 154. (b) Lal De, R.; Wolters, D.; Vahrenkamp, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1986**, *B41*, 283.

[11] Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1984**, *106*, 1495.

[12] Fenske, D.; Merzweiler, K. *Angew. Chem.* **1986**, *98*, 357; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 338.

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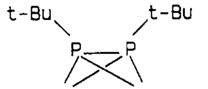

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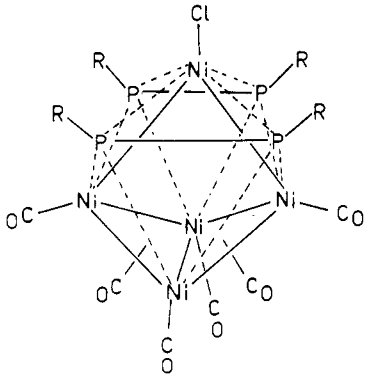
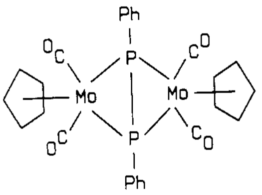


6 R = CH(SiMe$_3$)$_2$



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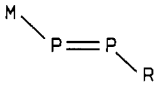

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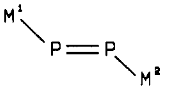

II

this paper we report full details on our synthetic approach to diphosphenes of the type I using transition-metal disilylphosphido complexes and ArPCl$_2$. We also report the X-ray structure analysis of $(\eta^5\text{-}C_5Me_5)(CO)_2FeP{=}PAr$ that exhibits the *E* stereochemistry at the P=P double bond.[13]

Experimental Section

General Information. Standard inert-atmosphere techniques were used for the manipulation of all reagents and reaction products. Infrared spectra were recorded on a Perkin-Elmer Model 597 spectrometer. The ^{1}H, ^{13}C, and ^{31}P NMR spectra were taken on a Varian XL 200 NMR spectrometer. Spectral standards were SiMe$_4$ (^{1}H, ^{13}C) and 85% H$_3$PO$_4$ (^{31}P). Chemical ionization mass spectra were recorded on a Varian MAT 312 spectrometer. Cryoscopical molecular weight determinations were performed in benzene under nitrogen. Elemental analyses were obtained from the Microanalytical Laboratory of the University Essen and from the Microanalytical Laboratory DORNIS and KOLBE, Mülheim, Germany.

Materials. The disilylphosphido complexes $(\eta^5\text{-}C_5Me_5)(CO)_2MP(SiMe_3)_2$ (M = Fe,[14] Ru,[15] Os[16]), and $(\eta^5\text{-}C_5H_5)(CO)(PPh_3)FeBr$[17] as well as the phosphine 2,4,6-*t*-Bu$_3$C$_6$H$_2$PCl$_2$ (ArPCl$_2$)[18] were prepared as described in the literature. All solvents were rigorously dried with an appropriate drying agent and distilled before use.

Preparation of Compounds. $(\eta^5\text{-}C_5H_5)(CO)(PPh_3)FeP(SiMe_3)_2$ (8d). To a suspension of 2.42 g (4.92 mmol) of $(\eta^5\text{-}C_5H_5)(PPh_3)(CO)FeBr$ in 50 mL of hexane was added 1.61 g (4.92 mmol) of solid LiP(SiMe$_3$)$_2$·2THF at +20 °C. The suspension was stirred for 2 h. The dark green solution was filtered and concentrated until the first appearance of dark green crystals. Then the solution was stored overnight at −28 °C. The mother liquor was decanted from black-green crystalline **8d**, and the product was dried in a vacuum: yield 1.50 g (52%) of green-black crystals; mp 85 °C dec; IR (cyclopentane) 1927 (s) cm^{-1} (ν(CO)); IR (Nujol) 3058 (w), 1908 (vs) (ν(CO)), 1482 (m), 1438 (s), 1258 (w), 1245 (m) (δ(Si(CH$_3$)$_3$), 1097 (m), 850 (s) and 835 (s) (ρ(Si-(CH$_3$)$_3$) and π (C–H(ring)), 830 (sh), 760 (m), 748 (m), 700 (s), 625 (m), 608 (s), 560 (s), 530 (s) cm^{-1}; ^{1}H NMR (C$_6$D$_6$, 22 °C) δ 0.38 (d, $^3J_{PH}$ = 3.5 Hz, 18 H, SiMe$_3$), 4.41 (s, 5 H, C$_5$H$_5$), 7.00–7.75 (m, 15 H, Ph); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 22 °C) δ 6.15 (d, $^2J_{PC}$ = 10.8 Hz, SiMe$_3$), 82.36 (d, $^2J_{PC}$ = 1.8H Hz, C$_5$H$_5$), 128.17 (s), 129.74 (d, J_{PC} = 1.9 Hz), 133.89 (dd, J_{PC} = 9.0 and 4.7 Hz), 137.11 (dd, J_{PC} = 41.5 and 2.5 Hz, *C*-phenyl), 222.67 (dd, J_{PC} = 33.4 and 4.4 Hz, FeCO); ^{31}P{^{1}H} (C$_6$D$_6$, 22 °C) δ −287.10 (d, $^2J_{PP}$ = 30.1 Hz, PSiMe$_3$), 64.94 (d, $^2J_{PP}$ = 30.1 Hz, PPh$_3$). Anal. Calcd for C$_{30}$H$_{38}$FeOP$_2$Si$_2$ (588.6): C, 61.22; H, 6.51; Fe, 9.49. Found: C, 60.97; H, 6.32; Fe, 9.34; mol wt, 594 (cryoscopically in benzene).

(*E*)-$(\eta^5\text{-}C_5Me_5)(CO)_2FeP{=}PAr$ (9a). Solid (2,4,6-tri-*tert*-butylphenyl)dichlorophosphine (ArPCl$_2$) (1.67 g, 4.83 mmol) was added to a solution of 2.05 g (4.83 mmol) of $(\eta^5\text{-}C_5Me_5)(CO)_2FeP(SiMe_3)_2$ in 40 mL of THF at 0 °C. The red-brown solution was stirred at 20 °C for 30 min, and the solvent was then removed under vacuum. The residue was dissolved in 25 mL of hexane and filtered. The ocher-yellow residue left in the filter was washed with hexane (2 × 3 mL) and dried under vacuum to yield 1.43 g (59%) of [(2,4,6-tri-*tert*-butylphenyl)diphosphenyl]dicarbonyl(pentamethylcyclopentadienyl)iron (**9a**): mp 165–167 °C; IR (cyclopentane) 2005 (s), 1956 (s) cm^{-1} (ν(CO)); IR (Nujol) 2025 (m), 1989 (vs), 1972 (m), 1946 (vs), 1915 (m) (ν(CO)), 1595 (w), 1365 (m), 1240 (w), 1218 (w), 1130 (w), 1078 (w), 1032 (w), 885 (w), 870 (w), 760 (w), 640 (w), 608 (w), 580 (s), 550 (w), 520 (w) cm^{-1}; ^{1}H NMR (C$_6$D$_6$, 22 °C) δ 1.33 (s, 9 H, *p*-*t*-Bu), 1.34 (s, 15 H, C$_5$(CH$_3$)$_5$), 1.73 (s, 18 H, *o*-*t*-Bu), 7.65 (s, 2 H, *m*-phenyl-H); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 22 °C) δ 9.32 (d, $^3J_{PC}$ = 5.6 Hz, C$_5$(*C*H$_3$)$_5$), 31.60 (s, *p*-C(*C*H$_3$)$_3$), 34.84 (s, *o*-C(*C*H$_3$)$_3$), 34.94 (s, *p*-*C*(CH$_3$)$_3$), 38.87 (s, *o*-*C*(CH$_3$)$_3$), 97.34 (s, *C*$_5$(CH$_3$)$_5$), 122.13 (s, *m*-phenyl-C), 148.55 and 152.32 (s and d, respectively, J_{PC} = 6.1 Hz, phenyl-C), 216.27 (d, $^2J_{PC}$ = 11.9 Hz, FeCO); ^{31}P{^{1}H} NMR (C$_6$D$_6$, 22 °C) δ 715.2 (d, $^1J_{PP}$ = 594.2 Hz, PFe), 553.5 (d, $^1J_{PP}$ = 594.2 Hz, PC). Anal. Calcd for C$_{30}$H$_{44}$FeO$_2$P$_2$ (554.5): C, 64.97; H, 8.01; Fe, 10.07. Found: C, 64.69; H, 7.98; Fe, 10.19; mol wt, 555 (MS/CI), 559 (cryoscopically in C$_6$H$_6$).

(*E*)-$(\eta^5\text{-}C_5Me_5)(CO)_2RuP{=}PAr$ (9b). Analogously, orange-yellow [(2,4,6-tri-*tert*-butylphenyl)diphosphenyl]dicarbonyl(pentamethylcyclopentadienyl)ruthenium (**9b**) (1.21 g, 67.5%) was synthesized from 1.035 g (2.99 mmol) of ArPCl$_2$ and 1.40 g (2.99 mmol) of $(\eta^5\text{-}C_5Me_5)(CO)_2RuP(SiMe_3)_2$ (**8b**) in 40 mL of THF: mp 169–170 °C; IR (cyclopentane) 2021 (s), 1968 (s) cm^{-1} (ν(CO)); IR (Nujol) 2032 (m), 2011 (vs), 1972 (m), 1956 (vs), 1925 (m) (ν(CO)), 1592 (w), 1365 (m), 1240 (w), 1218 (w), 1128 (w), 1078 (w), 1020 (w), 885 (w), 760 (w), 650 (w), 588 (w), 558 (s), 515 (m) cm^{-1}; ^{1}H NMR (C$_6$D$_6$, 22 °C) δ 1.33 (s, 9 H, *p*-*t*-Bu), 1.45 (s, 15 H, C$_5$(CH$_3$)$_5$), 1.75 (s, 18 H, *o*-*t*-Bu), 7.65 (s, 2 H, *m*-phenyl-H)); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 22 °C) δ 9.59 (d, $^3J_{PC}$ = 4.7 Hz, C$_5$(*C*H$_3$)$_5$), 31.61 (s, *p*-C(*C*H$_3$)$_3$), 34.90 (s, *o*-C(*C*H$_3$)$_3$), 34.94 (s, *p*-*C*(CH$_3$)$_3$), 38.92 (s, *o*-*C*(CH$_3$)$_3$), 101.05 (s, *C*$_5$(CH$_3$)$_5$), 122.17 (s, *m*-phenyl-C), 148.56 and 152.32 (s and d, respectively, J_{PC} = 7.8 Hz, C-phenyl), 202.05 (d, $^2J_{PC}$ = 13.9 Hz, RuCO); ^{31}P{^{1}H} NMR (C$_6$D$_6$, 22 °C) δ 676.5 (d, $^1J_{PP}$ = 597.1 Hz, PRu), 551.6 (d, $^1J_{PP}$ = 597.1 Hz, PC). Anal. Calcd for C$_{30}$H$_{44}$O$_2$P$_2$Ru (599.7): C, 60.08; H, 7.41. Found: C, 60.15; H, 7.36; mol wt, 600 (MS/CI), 589 (cryoscopically in C$_6$H$_6$).

Preparation of $(\eta^5\text{-}C_5Me_5)(CO)_2OsP{=}PAr$ (9c) and $(\eta^5\text{-}C_5Me_5)(CO)_2OsP[Ni(CO)_3]{=}PAr$ (10c). To a solution of 0.50 g (0.89 mmol) of $(\eta^5\text{-}C_5Me_5)(CO)_2OsP(SiMe_3)_2$ (8c) in 30 mL of THF was added 0.31 g (0.89 mmol) of ArPCl$_2$ at −30 °C. The reaction mixture was stirred for 1 h at 20 °C. Then the solution was cooled to −196 °C, and a large excess of Ni(CO)$_4$ was condensed into the flask. After warmup to room temperature the mixture was stirred for 2 h and thereafter freed from volatiles in a vacuum. The brown oily residue was extracted with 30 mL of hexane and filtered, and the filtrate was taken to dryness. The addition of 20 mL of ether was followed by filtration and concentration of the filtrate to ca. 5 mL. At −28 °C yellow-brown

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[13] Parts of our results have been reported in a preliminary communication: Weber, L.; Reizig, K. *Angew. Chem.* **1985**, *97*, 868; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 865.

[14] Weber, L.; Reizig, K.; Boese, R. *Chem. Ber.* **1985**, *118*, 1193.

[15] Weber, L.; Reizig, K.; Boese, R. *Organometallics* **1985**, *4*, 2097.

[16] Weber, L.; Bungardt, D. *J. Organomet. Chem.* **1986**, *311*, 269.

[17] Aris, K. R.; Brown, J. M.; Taylor, K. A. *J. Chem. Soc., Dalton Trans.* **1974**, 222.

[18] Yoshifuji, M.; Shima, I.; Inamoto, N.; Hirotsu, K.; Higuchi, T. *J. Am. Chem. Soc.* **1981**, *103*, 4587.

crystals of **10c** separated. The mother liquor was pipetted off, and the crystals were dried in a vacuum: yield 0.164 g (22%); mp 152 °C dec; IR (cyclopentane) 2070 (s), 2008 (vs), 1964 (s) (ν(CO), Ni(CO)$_3$), 2024 (s), 1988 (s), (ν(CO), Os(CO)$_2$); IR (Nujol) 2063 (m), 2015 (s), 1982 (vs), 1969 (s), 1590 (w), 1364 (w), 1264 (w), 1080 (w, br), 1042 (w, br), 805 (w) cm^{-1}; ^{1}H NMR (C$_6$D$_6$, 22 °C) δ 1.45 (s, 9 H, *p*-*t*-Bu), 1.65 (s, 15 H, C$_5$(CH$_3$)$_5$), 1.71 (s, 18 H, *o*-*t*-Bu), 7.68 (s, 2 H, *m*-phenyl-H); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 22 °C) δ 9.80 (s, C$_5$(*C*H$_3$)$_5$), 31.62 (s, *p*-C(*C*H$_3$)$_3$), 33.88 (d, $^4J_{PC}$ = 3.9 Hz, *o*-C(*C*H$_3$)$_3$), 35.23 (s, *p*-*C*(CH$_3$)$_3$), 38.81 (s, *o*-*C*(CH$_3$)$_3$), 98.75 (s, *C*$_5$(CH$_3$)$_5$), 123.16 (s), 149.41 (s), 151.25, 151.41 (*C*-aryl), 182.09 (d, $^2J_{PC}$ = 5.7 Hz, Os(CO)), 197.12 (d, $^2J_{PC}$ = 4.3 Hz, Ni(CO)); ^{31}P{^{1}H} NMR (C$_6$D$_6$, 22 °C) AB spin system δ_A 500.09, δ_B 495.64 (J_{AB} = 545.8 Hz). Anal. Calcd for C$_{33}$H$_{44}$NiO$_5$OsP$_2$ (831.6): C, 47.66; H, 5.34; Ni, 7.06. Found: C, 47.55; H, 5.42; Ni, 7.17.

(*E*)-(η^5-C$_5$H$_5$)(CO)(PPh$_3$)FeP=PAr (9d). A solution of 0.78 g (1.35 mmol) of (η^6-C$_5$H$_5$)(CO)(PPh$_3$)FeP(SiMe$_3$)$_2$ (**8d**) in 50 mL of THF was treated at 0 °C with 0.46 g (1.33 mmol) of solid ArPCl$_2$ and stirred for 30 min at room temperature. The color of the mixture rapidly changed from green to brown. After removal of volatiles in a vacuum, the brown residue was extracted with 50 mL of toluene and filtered, and the filtrate again was freed from solvent. The residue was extracted with hexane until the extracts remained colorless, and the combined extracts were concentrated to 25 mL. When stored overnight at −5 °C, a red-brown microcrystalline solid precipitated from which the mother liquor was decanted. Drying in a vacuum yielded 0.52 g (57%) of **9d** as a red-brown powder: mp 122 °C dec; IR (cyclopentane): 1947 (s), 1937 (vs) cm^{-1} (ν(CO)); IR (Nujol) 3060 (w), 1923 (vs) [ν(CO)], 1597 (w), 1440 (m), 1438 (m), 1392 (m), 1380 (m), 1363 (m), 1095 (m), 1005 (w), 880 (w), 845 (w), 834 (m) (π(CH)$_{ring}$) 755 (m), 750 (sh), 745 (w), 698 (s), 558 (s), 530 (s) cm^{-1}; ^{1}H NMR (C$_6$D$_6$, 22 °C) δ 1.30 (s, *p*-*t*-Bu), 1.64 (s, 18 H, *o*-*t*-Bu), 4.42 (d, J_{PH} = 0.9 Hz, 5 H, C$_5$H$_5$), 6.98 and 7.50 (m, 15 H, Ph), 7.60 (s, 2 H, *m*-H-aryl); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 22 °C) δ 31.60 (s, *p*-C(CH$_3$)$_3$), 34.58 (s) and 34.70 (s, *o*-C(*C*H$_3$)$_3$), 34.86 (s, *p*-*C*(CH$_3$)$_3$), 38.94 (s, *o*-*C*(CH$_3$)$_3$), 84.92 (s, C$_5$H$_5$), 122.07 (s), 129.83 (d, J_{PC} = 2.1 Hz), 133.53 (d, J_{PC} 8.9 Hz), 136.52 (s), 137.37 (s), 148.02 (s), 151.91 (d, J_{PC} = 6.4 Hz, C-phenyl and *C*-aryl), 220.0 (m, FeCO); ^{31}P{^{1}H} NMR δ 73.88 (dd, $^2J_{PP}$ = 19 Hz, $^3J_{PP}$ = 8.1 Hz, PPh$_3$), 561.95 (dd, $^1J_{PP}$ = 621.2 Hz, $^3J_{PP}$ = 8.1 Hz, P=*P*C), 765.35 (dd, $^1J_{PP}$ = 621.2 Hz, $^2J_{PP}$ = 19.7 Hz, Fe*P*=P). Anal. Calcd for C$_{42}$H$_{49}$FeOP$_3$ (718.6): C, 70.19; H, 6.87; Fe, 7.77. Found: C, 70.01; H, 7.09; Fe, 7.60; mol wt, 712 (cryoscopically in benzene).

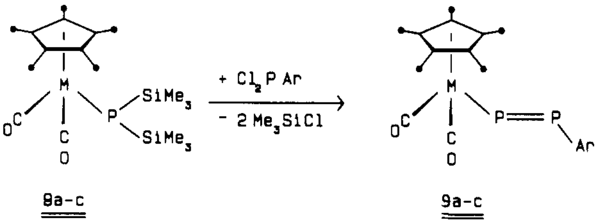
X-ray Structure Determination of [(*E*)-(η^5-C$_5$Me$_5$)(CO)$_2$FeP=PAr] (9a). Crystals of **9a** were grown from ether at 5 °C. An irregulary shaped crystal of the approximate dimensions 0.38 × 0.33 × 0.26 mm^3 was sealed in a glass capillary and mounted at room temperature on a Nicolet R3 four-circle diffractometer (Mo Kα radiation, graphite monochromator). The cell dimensions were determined by refinement of the setting angles of 25 reflections (20° ≤ 2θ ≤ 25°). The monoclinic lattice was established by oscillation photos (a = 12.414 (6) Å, b = 15.582 (7) Å, c = 20.347 (8) Å, β = 126.45 (3)°, V = 3166 (2) Å^3). The space group was determined to be $P2_1/c$ (Z = 4; D_{calcd} = 1.16 g/cm^3; μ = 5.96 cm^{-1}; ω-scan data collection of 4146 independent reflections (2θ_{max} = 45°), 3361 of which were treated as observed [$F_o \geq 3.5\sigma(F)$]. The structure was solved by direct methods, successive difference Fourier maps, and least-squares cycles. Crystallographic programs were those of SHELXTL[19] on a NOVA 3/12 computer with the atomic scattering factors taken as incorporated in the program. All non-hydrogen atoms were given anisotropical thermal displacement parameters. Those of the cyclopentadienyl methyl groups and the carbonyl ligands indicated a high disorder, which could not be resolved. The thermal ellipsoid point in a direction that is reasonable for this displacement, and ORTEP plot is available in the supplementary material. Cyclopentadienyl and arene rings were treated as rigid groups, as well as all hydrogen atoms. The latter were given the 1.2-fold isotropic temperature parameter of the equivalent anisotropic thermal parameter for the bonded C atom. The R values, based on the final model refined with 331 parameters, were $R = \sum(||F_o| - |F_c||/\sum|F_o|) = 0.068$ and $R_w = (\sum w||F_o| - |F_c||^2/\sum w|F_o|^2)^{1/2} = 0.079$, where $w^{-1} = (\sigma^2(F_o) + 1.27 \times 10^{-3}F_o^2)$. The maximum residual electron density was 0.65 e/Å^3 at a distance of 0.96 Å from Fe(1). For the last cycle the maximum and the mean shift to error were 0.065 and 0.003, respectively.

Results and Discussion

Satgé described the reaction between *tert*-butyldisilylphosphine and *tert*-butyldichlorophosphine as a method for the generation of reactive P=P double bonds (eq 1)[20] which was subsequently also used by Bickelhaupt.[21] We have extended this synthetic approach to disilylphosphido complexes of iron, ruthenium, and osmium as starting materials.

$$t\text{-BuP(SiMe}_3)_2 + t\text{-BuPCl}_2 \rightarrow 2\text{Me}_3\text{SiCl} + [t\text{-BuP}{=}\text{P-}t\text{-Bu}] \quad (1)$$

The iron and ruthenium compounds **8a,b** smoothly react with an equimolar amount of (2,4,6-tri-*tert*-butylphenyl)dichlorophosphine (ArPCl$_2$) in THF at 20 °C to give the orange-brown diphosphenes **9a,b**. The course of the reaction is easily monitored by ^{31}P NMR spectroscopy. The singlets of the starting materials are rapidly replaced by two doublets in the characteristic low-field region of diphosphenes. Possible intermediates of the reaction could not be detected. The compounds **9a,b** are conveniently isolated and are stable at 20 °C under N$_2$ atmosphere. This is, however, not the case with the corresponding osmium homologue **9c**. This complex is analogously formed from the reaction of (η^5-C$_5$Me$_5$)(CO)$_2$OsP(SiMe$_3$)$_2$ and ArPCl$_2$ in THF at 20 °C and is stable in solution for several hours as evidenced by ^{31}P NMR spectroscopy (vide infra). Attempts to isolate this compound resulted in decomposition.



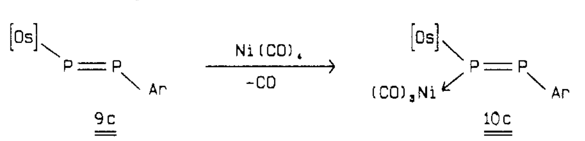
(2)

Ar=2,4,6-tri-t-butylphenyl

● = Me

9	M
a	Fe
b	Ru
c	Os

When a freshly prepared THF solution of **9c** is treated with an excess of Ni(CO)$_4$, the diphosphene is trapped as the Ni(CO)$_3$ complex **10c** (eq 3). A considerable steric congestion provided by the substituents at the P=P function is crucial for the existence of kinetically stabilized diphosphenes.[2,21] In keeping with this finding preliminary



(3)

[Os] = (C$_5$Me$_5$)(CO)$_2$Os

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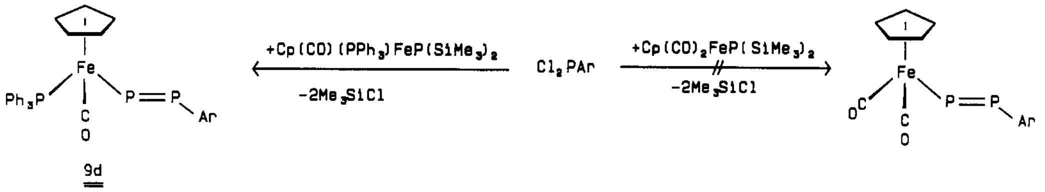
[19] Sheldrick, G. M. SHELXTL, ein komplettes Programm zum Lösen, Verfeinern und Darstellen von Kristallstrukturen aus Beugungsdaten, Universität Göttingen, 1981.

[20] Escudie, J.; Couret, C.; Andriamizaka, J. D.; Satgé, J. *J. Organomet. Chem.* **1982**, *228*, C76.

[21] Smit, C. N.; van der Knaap, T. A.; Bickelhaupt, F. *Tetrahedron Lett.* **1983**, *24*, 2031.

Scheme I



studies show that no diphosphene can be obtained from the reaction of **8a,b** with mesityldichlorophosphine. Instead metal-substituted cyclotriphosphines and cyclotetraphosphines are obtained.[22]

The steric situation at the metal center also influences the course of the reaction. Thus, when the bulky C_5Me_5 ring in **8a,b** is replaced by the smaller C_5H_5 ligand, the synthesis of diphosphenes fails. The introduction of a triphenylphosphine at the iron again provides sufficient steric congestion at the metal center so that the transformation under discussion proceeds successfully (Scheme I). The phosphines $Cl_2PN(SiMe_3)_2$, $Cl_2PN(t\text{-}Bu)(SiMe_3)$, and $Cl_2PC(SiMe_3)_3$ do not react with the disilylphosphido complexes **8a,b**.

The products **9a–d** were initially characterized by elemental analyses and spectroscopic methods (IR, ^1H, ^{13}C, and ^{31}P NMR, MS). Cryoscopic molecular weight determinations in benzene as well as chemical ionization mass spectra revealed the monomeric character of the compounds. The presence of unsymmetrically substituted diphosphenes is confirmed unequivocally by the ^{31}P NMR spectra of **9a–c**. Two doublets at very low field (**9a** (C_6D_6): δ_A 715.2 (d), δ_X 553.5 (d, $^1J_{P_AP_X}$ = 594.2 Hz); **9b** (C_6D_6): δ_A 676.5 (dd), δ_X 551.6 (d, $^1J_{P_AP_X}$ = 597.1 Hz); **9c** (THF): δ_A 631.99 (d), δ_X 543.19 (d, $^1J_{P_AP_X}$ = 583.9 Hz)) with very large coupling constants are diagnostic for unsymmetrical diphosphenes.[2] The largest low-field shift to date for uncomplexed diphosphenes was recorded for $(Me_3Si)_3CP{=}C(SiMe_3)_3$ (δ 599.7),[23] and the largest coupling constant up to now for an unsymmetrical diphosphene was reported by Niecke et al. for $(Me_3Si)_2NP{=}PN(t\text{-}Bu)(SiMe_3)$ ($^1J_{PP}$ = 670 Hz).[24] In our diphosphenes **9** the metalated phosphorus atom is significantly shifted upfield in going from Fe to Os, whereas the phenyl-substituted phosphorus is far less affected by the nature of the metal. Due to the coupling of the P=P system with the phosphorus of the triphenylphosphine ligand in **9d** the low-field resonances at δ 765.35 and 561.95 appear as double doublets with a large coupling of ^1J = 621.2 Hz. In the $Ni(CO)_3$ derivative **10c** the phosphorus nuclei of the still unsupported P=P bond give rise to an AB spectrum with δ_A 500.09 and δ_B 495.64 ($^1J_{AB}$ = 545.8 Hz). The osmium-bound P atom experiences a high-field shift of about 130 ppm, whereas the other one is only shifted by ca. 50 ppm to high field. This is in accordance with the coordination of Ni and Os to the same phosphorus. The $M(CO)_2$ groups of **9a–c** give rise to two intense ν(CO) bands at 2005 and 1956 cm^{-1} (**9a**), 2021 and 1968 cm^{-1} (**9b**), and 2008 and 1956 (**9c**). In the starting materials **8a** (1990, 1945 cm^{-1}), **8b** (2012, 1953 cm^{-1}), and **8c** (1994, 1941 cm^{-1}) these bands appear at considerably lower wavenumbers, which reflects the more pronounced σ-donor/π-acceptor capability of the educts.

Table I. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters (Å^2 $\times$ 10^3) for 9a

atom	x	y	z	U^a
Fe(1)	1606 (1)	8919 (1)	2967 (1)	66 (1)
P(1)	3004 (1)	8719 (1)	4334 (1)	60 (1)
P(2)	2262 (1)	7797 (1)	4666 (1)	61 (1)
C(1)	1900 (15)	7856 (6)	2902 (5)	196 (12)
O(1)	2146 (16)	7148 (4)	2856 (6)	328 (16)
C(2)	249 (7)	8756 (7)	2968 (5)	159 (6)
O(2)	−702 (5)	8680 (7)	2979 (5)	260 (7)
C(3)	912 (4)	9475 (3)	1846 (2)	83 (4)
C(4)	720	10059	2304	93 (5)
C(5)	1994	10250	3039	89 (5)
C(6)	2974	9784	3035	85 (4)
C(7)	2305	9306	2298	85 (5)
C(8)	−174 (12)	9153 (8)	1024 (5)	198 (8)
C(9)	−597 (11)	10433 (9)	2024 (9)	217 (13)
C(10)	2327 (16)	10874 (7)	3688 (7)	223 (17)
C(11)	4445 (8)	9834 (9)	3652 (7)	201 (8)
C(12)	2869 (15)	8758 (7)	1949 (9)	218 (18)
C(14)	3408 (2)	8378 (2)	6272 (2)	46 (2)
C(15)	4439	8465	7103	51 (3)
C(16)	5581	7953	7468	49 (3)
C(17)	5692	7354	7002	51 (3)
C(18)	4661	7267	6170	50 (3)
C(13)	3519	7779	5805	46 (2)
C(19)	2123 (4)	8936 (3)	5971 (3)	56 (3)
C(20)	864	8382	5516	111 (6)
C(21)	1947 (6)	9683 (4)	5436 (4)	86 (4)
C(22)	2215 (8)	9350 (7)	6672 (5)	132 (6)
C(23)	6751 (5)	8066 (3)	8383 (3)	60 (3)
C(24)	6950	7243	8827	134 (6)
C(25)	8061 (6)	8238 (6)	8474 (4)	116 (5)
C(26)	6572 (9)	8816 (7)	8756 (5)	161 (6)
C(27)	4871 (5)	6508 (3)	5761 (3)	64 (3)
C(28)	3570	5992	5173	108 (5)
C(29)	5419 (10)	6838 (5)	5294 (6)	124 (8)
C(30)	5819 (7)	5824 (4)	6381 (4)	96 (5)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table II. Selected Bond Lengths (Å) of 9a

Fe(1)–P(1)	2.260 (1)	Fe(1)–C(1)	1.717 (10)
Fe(1)–C(2)	1.705 (11)	Fe(1)–C(3)	2.089 (4)
Fe(1)–C(4)	2.103 (5)	Fe(1)–C(5)	2.115 (5)
Fe(1)–C(6)	2.108 (6)	Fe(1)–C(7)	2.092 (6)
P(1)–P(2)	2.027 (3)	P(2)–C(13)	1.873 (3)
C(1)–O(1)	1.164 (14)	C(2)–O(2)	1.199 (14)

Compound **10c** displays three ν(CO) bands for the $Ni(CO)_3$ moiety (2070, 2008, 1964 cm^{-1}) and two bands at 2024 and 1958 cm^{-1} due to the $Os(CO)_2$ group.

X-ray Structure Analysis of 9a. The X-ray structure analysis of **9a** fully confirms the conclusions derived from analyses and spectroscopic data. The results of the structural determinations are shown in Figure 1. Positional parameters for the complex are given in Table I, and derived distances and angles are presented in Tables II and III, respectively.

The analysis clearly confirms that **9a** contains a [P=P—Ar] unit linked to the metal through a Fe—P covalent bond. The ligand could be considered as one leg in a distorted three-legged piano-stool arrangement. The distortion is evident by the three different angles the ligands form with the iron atom (P(1)–Fe(1)–C(1) = 85.4 (3)°;

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(22) Weber, L.; Bungardt, D. *Chem. Ber.*, in press.

(23) (a) Cowley, A. H.; Kilduff, J. E., Newman, T. H.; Pakulski, M. *J. Am. Chem. Soc.* **1982**, *104*, 5820. (b) Couret, C., Escudie, J.; Satgé, J. *Tetrahedron Lett.* **1982**, *23*, 4941. (c) Schmidt, H.; Wirkner, C.; Issleib, K. *Z. Chem.* **1983**, *23*, 67.

(24) Niecke, E.; Rüger, R.; Lysek, M.; Pohl, S.; Schoeller, W. *Angew. Chem.* **1983**, *95*, 495; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 486; *Angew. Chem. Suppl.* **1983**, 639.

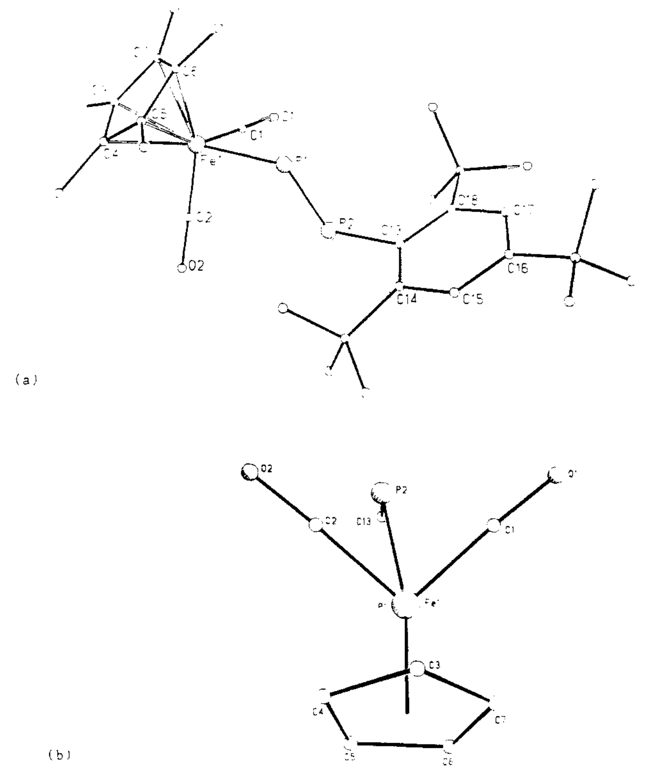
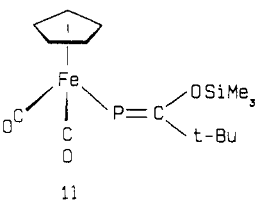


Figure 1. Two views of the molecular structure of (η^5-C_5Me_5)$(CO)_2FeP{=}PC_6H_2$-*t*-Bu-2,4,6 (**9a**). (b) Approximates a Newman projection down the Fe(1)P(1) bond (methyl groups at the ring ligand and the complete aryl substituent at P(2) are omitted for clarity).

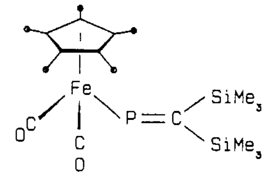
Table III. Bond Angles (deg) of 9a

P(1)-Fe(1)-C(1)	85.4 (3)	P(1)-Fe(1)-C(2)	90.9 (3)
C(1)-Fe(1)-C(2)	96.4 (7)	P(1)-Fe(1)-C(3)	156.6 (1)
C(1)-Fe(1)-C(3)	106.5 (4)	C(2)-Fe(1)-C(3)	107.2 (3)
P(1)-Fe(1)-C(4)	129.2 (1)	C(1)-Fe(1)-C(4)	145.0 (3)
C(2)-Fe(1)-C(4)	89.2 (4)	P(1)-Fe(1)-C(5)	94.2 (1)
C(1)-Fe(1)-C(5)	154.2 (7)	C(2)-Fe(1)-C(5)	109.3 (4)
P(1)-Fe(1)-C(6)	90.5 (1)	C(1)-Fe(1)-C(6)	114.9 (6)
C(2)-Fe(1)-C(6)	148.6 (4)	P(1)-Fe(1)-C(7)	121.9 (1)
C(1)-Fe(1)-C(7)	92.2 (6)	C(2)-Fe(1)-C(7)	146.7 (3)
Fe(1)-P(1)-P(2)	109.8 (1)	P(1)-P(2)-C(13)	102.4 (1)
Fe(1)-C(1)-O(1)	177.0 (18)	Fe(1)-C(2)-O(2)	177.0 (11)
Fe(1)-C(3)-C(4)	70.7 (2)	Fe(1)-C(3)-C(7)	70.2 (2)
Fe(1)-C(3)-C(8)	127.0 (6)	Fe(1)-C(4)-C(3)	69.7 (1)
Fe(1)-C(4)-C(5)	70.8 (1)	Fe(1)-C(4)-C(9)	127.6 (7)
Fe(1)-C(5)-C(4)	69.9 (1)	Fe(1)-C(5)-C(6)	70.1 (2)
Fe(1)-C(5)-C(10)	129.4 (7)	Fe(1)-C(6)-C(5)	70.6 (2)
Fe(1)-C(6)-C(7)	69.6 (1)	Fe(1)-C(6)-C(11)	129.0 (6)
Fe(1)-C(7)-C(3)	70.0 (1)	Fe(1)-C(7)-C(6)	70.8 (1)
Fe(1)-C(7)-C(12)	128.8 (7)	P(2)-C(13)-C(14)	119.0 (1)
P(2)-C(13)-C(18)	120.2 (1)		

C(1)-Fe(1)-C(2) = 96.4 (7)°; P(1)-Fe(1)-C(2) = 90.9 (3)°). Two legs of the piano stool are represented by terminal carbonyl groups. The most interesting structural feature of **9a** is the geometry of the novel diphosphenyl ligand, which is attached to the iron via a Fe-P single bond [2.260 (1) Å]. In **11** and **12** the corresponding Fe-P bond lengths are found to be 2.298 (1)[25] and 2.256 (2)[26] Å, respectively.

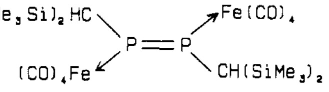


11



12

In the diphosphene complex **13** the Fe-P distance is considerably shorter (2.226 (1) Å[28]). Both phosphorus



13

atoms are linked by a double bond of 2.027 (3) Å which compares well with the P=P distance of 2.034 (2) Å found in Yoshifuji's diphosphene $[2,4,6\text{-}t\text{-}Bu_3C_6H_2P]_2$.[18] Both substituents at the P=P double bond adapt the *E* configuration, which is found in most stable diphosphenes. The bond angle P(1)-P(2)-C(13) of 102.4 (1)° is comparable with the one in $[2,4,6\text{-}t\text{-}Bu_3C_6H_2P]_2$ (102.8 (1)°), whereas the angle Fe(1)-P(1)-P(2) (109.8 (1)°) is markedly widened. The atoms Fe(1), P(1), P(2), and C(13) are arranged within a plane (torsion angle = -177.5°). This plane encloses an angle of 92.1° with the plane defined by the aryl ring. As it is evident from the torsion angles C(1)-Fe(1)-P(1)-P(2) (-59.9°) and C(2)-Fe(1)-P(1)-P(2) (36.5°), the plane defined by P(1), P(2), and C(13) does not bisect the triangle formed by the atoms Fe(1), C(1), and C(2) (see also Figure 1b), which gives a Newman projection along the Fe(1)-P(1) bond). The iron-carbon distances to the ring ligand vary from 2.089 (4) to 2.115 (5) Å, and the iron atom is located 1.720 Å underneath the middle of this ring.

The title compounds can thus be viewed as transition-metal-substituted diphosphenes or as the first diphosphenyl complexes. They are accordingly the phosphorus homologues of those diazenyl complexes in which the ligand functions as a 1e donor and in which, therefore, a doubly bent N—N=N—R geometry is present.[28]

Acknowledgment. Our work was generously supported by the Deutsche Forschungsgemeinschaft, Bonn, the Fonds der Chemischen Industrie, Frankfurt, the Degussa AG, Hanau, and the BASF, Ludwigshafen, Germany. This assistance is gratefully acknowledged.

Supplementary Material Available: Complete listings of atomic coordinates, anisotropic thermal parameters, bond lengths, and bond angles and an ORTEP plot for **9a** (6 pages); a listing of structure factor amplitudes for **9a** (20 pages). Ordering information is given on any current masthead page.

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[25] (a) Weber, L.; Reizig, K.; Boese, R.; Polk, M. *Angew. Chem.* **1985**, *97*, 583; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 604. (b) Weber, L.; Reizig, K.; Frebel, M.; Boese, R.; Polk, M. *J. Organomet. Chem.* **1986**, *306*, 105.

[26] Gudat, D.; Niecke, E.; Arif, A. M.; Cowley, A. H.; Quashie, S. *Organometallics* **1986**, *5*, 593.

[27] Flynn, K. M.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1983**, *105*, 2085.

[28] (a) Gaughan, A. P.; Ibers, J. A. *Inorg. Chem.* **1975**, *14*, 352. (b) Krogsrud, S.; Ibers, J. A. *Inorg. Chem.* **1975**, *14*, 2298. (c) Cobbledick, R. E.; Einstein, F. W. B.; Farell, N.; Gilchrist, A. B.; Sutton, D. *J. Chem. Soc., Dalton Trans.* **1977**, 373.