Organometallics **2004,** *23,* 2541−2551

Synthesis, Structures, and Electrochemistry of Group 6 Aminocarbenes with a P-Chelating 1′-(Diphenylphosphino)ferrocenyl Substituent

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Received January 15, 2004

Ferrocene amides $Ph_2PfcC(O)NR_2$ (**1**; fc = ferrocene-1,1′-diyl, NR_2 = NEt_2 (**a**), morpholin-4-yl (**b**)) react with $[Cr(CO)_5]^{2-}$ in the presence of Me_3SiCl to give easily separable mixtures of the respective P-chelated carbene $[Cr(CO)_4(Ph_2PfcC(NR_2)\text{-}\kappa^2C^1,P)]$ (**2**) and a phosphine complex, $[Cr(CO)_5(\mathbf{1}\text{-}\kappa P)]$ (**3**). A similar reaction between **1a** and $[W(CO)_5]^{2-}$ is more complex, affording a mixture of the nonchelated carbene $[Cr(CO)_4\{Ph_2PfcC(NEt)_2\text{-}\kappa C^1\}]$ (**5**), trimetallic carbene $[(\mu\text{-}1\kappa C^1,2\kappa P\text{-}Ph_2PfcC(NEt_2))\{W(CO)_5\}_2]$ (**6**), and the phosphine complex $[W(CO)_5\text{-}\{\mathbf{1a}\text{-}\kappa P\}]$ (**4**). Removal of **4** by chromatography and heating the mixture of **5** and **6** in toluene gives another mixture containing carbene analogous to **2**, $[W(CO)_4(Ph_2PfcC(NEt_2)\text{-}\kappa^2C^1,P)]$ (**7**), unreacted **6**, and $[W(CO)_5\{Ph_2PfcCHO\text{-}\kappa P\}]$ (**8**) as a decomposition product. In contrast, the reaction of **1a** with the iron carbonylate $[Fe(CO)_4]^{2-}$ under identical conditions yields solely $[Fe(CO)_4\{\mathbf{1a}\text{-}\kappa P\}]$ (**9**). All compounds except for **5** were isolated and characterized by spectral methods. The structures of **2a**·CH_2Cl_2, **2b**, **6**·$CHCl_3$, **7**, and **9** were determined by single-crystal X-ray diffraction. An electrochemical study showed that whereas compounds **1** and **3** behave as a simple system (ferrocene) and two localized redox systems (ferrocene and chromium), respectively, carbenes **2** are electronically delocalized systems, where the redox changes probably occur in the whole molecule.

Introduction

Compounds combining different organometallic moieties and their physicochemical properties have attracted considerable attention. The first ferrocenylated group 6 metal Fischer-type carbenes, $[(OC)_5M{=}C(Fc)(OR)]$[1] and $[(OC)_5M{=}C(Fc)(NR_2)]$,[1c] where M = Cr, Mo, W; Fc = ferrocenyl, and R is usually an alkyl group, were synthesized shortly after the first article concerning these types of compounds appeared.[2] Since then, other ferrocene carbenes have been synthesized and these carbenes have been converted to their respective carbynes,[3] applied in the synthesis of ferrocenylated organic molecules,[4] and studied as push−pull nonlinear optical materials (Scheme 1).[5] However, the chemistry of ferrocene carbenes bearing other functional group(s) at the ferrocene unit remains unexplored. In 1982, Herrmann and Ugi[6] reported the unexpected products resulting from the reaction of tungsten hexacarbonyl and (R,R_p)-1-{1-(dimethylamino)ethyl}-2-lithioferrocene.[7] Three years later, Cullen et al.[8] described the use of a functionalized lithium reagent, 1′-(diphenylphosphino)-ferrocenyllithium (**I**, Scheme 1),[9] in the procedure originally developed for the preparation of Fischer-type alkoxycarbenes to afford a mixture of chelated ferrocene methoxycarbenes **II** (M = Cr, W; 20−40%) and zwitterionic compounds **III** (10−20%).

More recently, we reported the carboxylation of **I** with carbon dioxide, providing 1′-(diphenylphosphino)ferrocenecarboxylic acid, $[Fe(\eta^5\text{-}C_5H_4PPh_2)\{\eta^5\text{-}C_5H_4CO_2H\}]$

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(1) (a) Connor, J. A.; Jones, E. M.; Lloyd, J. P. *J. Organomet. Chem.* **1970**, *24*, C20. (b) Moser, G. A.; Fischer, E. O.; Rausch, M. D. *J. Organomet. Chem.* **1971**, *27*, 379. (c) Connor, J. A.; Lloyd, J. P. *J. Chem. Soc., Dalton Trans.* **1972**, 1470 (the aminocarbenes were synthesized from the respective alkoxycarbenes by reacting with secondary amines).

(2) Fischer, E. O.; Maasböl, A. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 580.

(3) (a) Fischer, E. O.; Schluge, M.; Besenhard, J. O.; Friedrich, P.; Huttner, G.; Kreissl, F. R. *Chem. Ber.* **1978**, *111*, 3530. (b) Fischer, E. O.; Gammel, F. J.; Besenhard, J. O.; Frank, A.; Neugebauer, D. *J. Organomet. Chem.* **1980**, *191*, 261.

(4) Selected examples: (a) Connor, J. A.; Lloyd, J. P. *J. Chem. Soc., Dalton Trans.* **1973**, 17. (b) Dötz, K. H.; Dietz, R.; Neugebauer, D. *Chem. Ber.* **1979**, *112*, 1486. (c) Barluenga, J.; Fernández-Acebes, A.; Trabanco, A. A.; Flórez, J. *J. Am. Chem. Soc.* **1997**, *119*, 7591. (d) Mongin, C.; Ortin, Y.; Lugan, N.; Mathieu, R. *Eur. J. Inorg. Chem.* **1999**, 739. (e) Zora, M.; Güngör, E. Ü. *Tetrahedron Lett.* **2001**, *422*, 4733. (f) Zora, M.; Yucel, B.; Peynircioglu, N. B. *J. Organomet. Chem.* **2002**, *656*, 11.

(5) (a) Jayaprakash, K. N.; Ray, P. C.; Matsuoka, I.; Bhadbhade, M. M.; Puranik, V. G.; Das, P. K.; Nishihara, H.; Sarkar, A. *Organometallics* **1999**, *18*, 3851. For similar compounds see, e.g.: (b) Macomber, D. W.; Madhukar, P.; Rogers, R. D. *Organometallics* **1989**, *8*, 1275. (c) Briel, O.; Fehn, A.; Beck, W. *J. Organomet. Chem.* **1999**, *578*, 247.

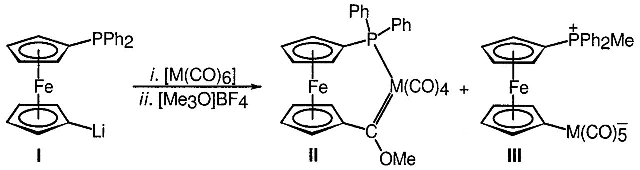
(6) Herrmann, R.; Ugi, I. *Angew. Chem.* **1982**, *94*, 798.

(7) Marquarding, D.; Klusacek, H.; Gokel, G.; Hoffmann, P.; Ugi, I. *J. Am. Chem. Soc.* **1970**, *92*, 5389.

(8) Butler, I. R.; Cullen, W. R.; Einstein, F. W. B.; Willis, A. C. *Organometallics* **1985**, *4*, 603.

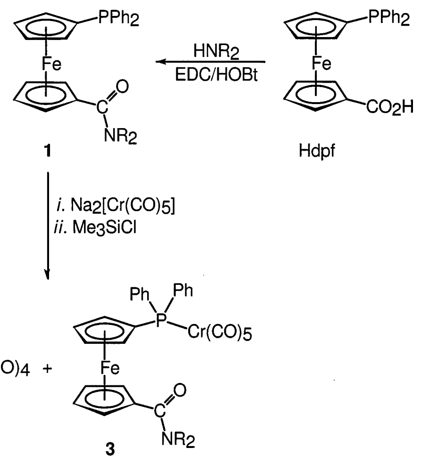
10.1021/om040007f CCC: $27.50

Scheme 1



(Hdpf),[10] and studied the coordination chemistry[11] and further synthetic utility[12] of this organometallic carboxyphosphine ligand. We have shown that Hdpf can act as a chelating ligand (as the dpf$^-$ anion in [Rh(L)(CO)(dpf-κ^2O,P)][11c]) and that in complexes with P-coordinated Hdpf the ferrocene unit and the metal center are electronically coupled.[11a] Since some 1,1′-chelating ferrocene ligands bring the ferrocene iron and the ligated metal into proximity, which allows for a direct donation from the electron-rich iron atom to the chelated metal (Fe→M),[13] we decided to synthesize the Hdpf amides $[Fe(\eta^5\text{-}C_5H_4PPh_2)\{\eta^5\text{-}C_5H_4C(O)NR_2\}]$ (**1**) and convert them into so far unknown, P-chelating ferrocene aminocarbenes analogous to **II**. In this contribution we report on the characterization, solid-state structures, and electrochemistry of the products arising from the reaction of chromium, tungsten, and iron carbonylate salts and 1′-(diphenylphosphino)ferrocene carboxamides.

Scheme 2[a]



[a] Legend: $NR_2 = NEt_2$ (**a**), morpholin-4-yl (**b**); EDC = *N*-[3-(dimethylamino)prop-1-yl]-*N*′-ethylcarbodiimide; HOBt = 1-hydroxy-1,2,3-benzotriazole.

Results and Discussion

Synthesis and Characterization of Amides and Chromium Complexes. The amides $Ph_2PfcC(O)NR_2$ (fc = ferrocene-1,1′-diyl; $NR_2 = NEt_2$ (**1a**), morpholin-4-yl (**1b**)) were obtained by amidation of Hdpf[10] with diethylamine and morpholine in nearly quantitative yields as viscous orange oils, which solidify upon standing to rusty brown, somewhat waxy solids. The amides were subsequently reacted with the carbonylate salts $[M(CO)_5]^{2-}$ (M = Cr, W) generated in situ[14] and an excess of Me_3SiCl, as reported previously by Hegedus et al.[15] The reaction of **1a** with $[Cr(CO)_5]^{2-}$ (Scheme 2) proceeded with the formation of two major products, which were separated by column chromatography and characterized as the P-chelated carbene **2a** (46%) and the phosphine carbonyl complex **3a** (37%). A similar reaction with the amide **1b** afforded a pair of analogous compounds, **2b** (19%) and **3b** (38%).

The chelated carbenes **2a** and **2b** were obtained as bright orange crystalline solids. They are fairly stable when stored as solids in the dark but decompose in daylight and in solution. The carbenes lack typical amide $\nu_{C=O}$ bands in their IR spectra and show characteristic low-field signals in the ^{13}C NMR spectra due to the carbene carbons (δ_C ca. 280) split into doublets by the phosphorus of the phosphine group ($^2J_{PC} = 13$ Hz). In addition, the ^{13}C NMR spectra show a markedly downfield-shifted, phosphorus-coupled signal of the ferrocene C_{ipso} attached to the carbene carbon (cf. δ_C 109.24 (d, $^3J_{PC} = 5$ Hz) for **2a** and 81.32 (s) for **3a**) and three signals due to the carbonyl ligands, as expected for an asymmetric *cis*-$[Cr(L^1)(L^2)(CO)_4]$ complex. In the ^{31}P NMR spectra **2a** and **2b** exhibit singlets shifted significantly downfield from those of the parent amides and also the phosphine complexes **3a** and **3b** (δ_P 58.1 (**2a**), 58.5 (**2b**)). The structures of **2a** and **2b** were corroborated by X-ray crystallography (see below).

The side products **3a** and **3b** are rusty orange, noncrystallizing solids, showing strong amide carbonyl

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[9] **I** can be prepared either by opening of the strained ferrocenophane ring in (ferrocene-1,1′-diyl)phenylphosphine[9a,b] with phenyllithium[9b,c] or, alternatively, by a stepwise metalation/functionalization of 1,1′-dibromoferrocene.[9d,e] Prior to the report concerning compounds **II** and **III**, reagent **I** has been utilized in the synthesis of ferraphosphinoferrocenophanes.[9f,g] (a) Osborne, A. G.; Whiteley, R. H.; Meads, R. E. *J. Organomet. Chem.* **1980**, *193*, 345. (b) Seyferth, D.; Withers, H. P., Jr. *Organometallics* **1982**, *1*, 1275. (c) Seyferth, D.; Withers, H. P., Jr. *J. Organomet. Chem.* **1980**, *185*, C1. (d) Butler, I. R.; Davies, R. L. *Synthesis* **1996**, 1350. (e) Dong, T.-Y.; Lai, L.-L. *J. Organomet. Chem.* **1996**, *509*, 131. (f) Butler, I. R.; Cullen, W. R. *Organometallics* **1984**, *3*, 1846. (g) Butler, I. R.; Cullen, W. R.; Rettig, S. J. *Organometallics* **1987**, *6*, 872.

[10] Podlaha, J.; Štěpnička, P.; Císařová, I.; Ludvík, J. *Organometallics* **1996**, *15*, 543.

[11] Representative examples: (a) Štěpnička, P.; Gyepes, R.; Lavastre, O.; Dixneuf, P. H. *Organometallics* **1997**, *16*, 5089. (b) Štěpnička, P.; Podlaha, J.; Gyepes, R.; Polášek, M. *J. Organomet. Chem.* **1998**, *552*, 293. (c) Štěpnička, P.; Císařová, I. *J. Chem. Soc., Dalton Trans.* **1998**, 2807. (d) Štěpnička, P.; Gyepes, R.; Podlaha, J. *Collect. Czech. Chem. Commun.* **1998**, *63*, 64. (e) Štěpnička, P.; Císařová, I.; Podlaha, J.; Ludvík, J.; Nejezchleba, M. *J. Organomet. Chem.* **1999**, *582*, 319. For other ferrocene phosphino carboxylic acids, see the following. (f) Zhang, T. Shimanuki, T. Kida, Y. Nakatsuji, I. Ikeda, I. *J. Org. Chem.* **1999**, *64*, 6247 and references cited therein (esters and amides). (g) You, S.-L.; Hou, X.-L.; Dai, L.-X.; Cao, B.-X.; Sun, J. *Chem. Commun.* **2000**, 1933. (h) Longmire, J. M.; Wang, B.; Zhang, X.; *Tetrahedron Lett.* **2000**, *41*, 5435. (i) Štěpnička, P. *New J. Chem.* **2002**, *26*, 567. (j) Štěpnička, P.; Císařová, I. *Organometallics* **2003**, *22*, 1728.

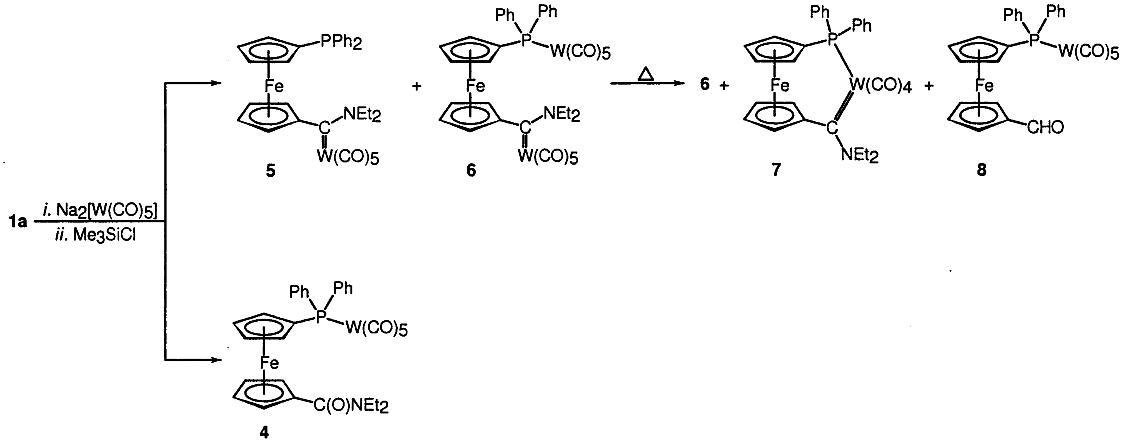
[12] So far, Hdpf has been used in the synthesis of ferrocene oxazolines[12a,b] and [1′-(diphenylphosphino)ferrocenyl]methanol:[12c] (a) Zhang, W.; Yoneda, Y.; Kida, T.; Nakatsuji, Y.; Ikeda, I. *Tetrahedron: Asymmetry* **1998**, *9*, 3371 (as Me ester). (b) Drahoňovský, D.; Císařová, I.; Štěpnička, P.; Dvořáková, H.; Maloň, P.; Dvořák, D. *Collect. Czech. Chem. Commun.* **2001**, *66*, 588. (c) Štěpnička, P.; Baše, T. *Inorg. Chem. Commun.* **2001**, *4*, 682.

[13] The Fe→M dative bond has been observed in complexes with chelating 1,1′-dichalcogenolatoferrocene(2−),[13a−e] 1,1′-bis(diphenylphosphino)ferrocene[13f,g] and also with some ferrocene diamide[13h] and bis(pyridyl)[13i] ligands. (a) Seyferth, D.; Hames, B. W.; Rucker, T. G.; Cowle, M.; Dickson, R. S. *Organometallics* **1983**, *2*, 472. (b) Cowie, M.; Dickson, R. S. *J. Organomet. Chem.* **1987**, *326*, 269. (c) Akabori, S.; Kumagai, T.; Shirahige, T.; Sato, S.; Kawazoe, K.; Tamura, C.; Sato, M. *Organometallics* **1987**, *6*, 526. (d) Akabori, S.; Kumagai, T.; Shirahige, T.; Sato, S.; Kawazoe, K.; Tamura, C.; Sato, M. *Organometallics* **1987**, *6*, 2105. (e) Takemoto, S.; Kuwata, S.; Nishibayashi, Y.; Hidai, M. *Inorg. Chem.* **1998**, *37*, 6428. (f) Sato, M.; Sekino, M.; Akabori, S. *J. Organomet. Chem.* **1988**, *344*, C31. (g) Sato, M.; Shigeta, H.; Sekino, M.; Akabori, S. *J. Organomet. Chem.* **1993**, *458*, 199. (h) Shafir, A.; Rheingold, J. *J. Am. Chem. Soc.* **2001**, *123*, 9212. (i) Enders, M.; Kohl, G.; Pritzkow, H. *Organometallics* **2002**, *21*, 1111.

[14] Borel, C.; Hegedus, L. S.; Krebs, J.; Satoh, Y. *J. Am. Chem. Soc.* **1987**, *109*, 1101.

[15] (a) Imwinkelried, R.; Hegedus, L. S. *Organometallics* **1988**, *7*, 702. (b) Schwindt, M. A.; Lejon, T.; Hegedus, L. S. *Organometallics* **1990**, *9*, 2814.

Scheme 3

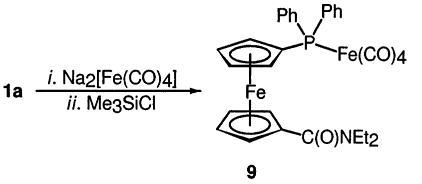


stretching bands in the IR spectra (**3a**, 1614 cm^{-1}; **3b**, 1623 cm^{-1}). The ^{1}H and ^{13}C NMR spectra of **3** are indicative of unchanged carboxamide groups and display resonances due to carbonyl ligands (^{13}C NMR) at positions nearly identical with those of [Cr(CO)$_5$(Hdpf-*κP*)].[16] Likewise, the ^{31}P NMR signals (δ_P 47.3 for **3a** and **3b**) compare nicely to those of [Cr(CO)$_5$(Hdpf-*κP*)] (δ_P 47.7), thus supporting the formulation of **3** as [Cr(CO)$_5$(**1**-*κP*)], where the amides behave as simple phosphine ligands.

Preparation of Tungsten Analogues. In comparison to the chromium system, the reactions occurring with tungsten carbonylate under analogous conditions are more complex. The reaction of [W(CO)$_5$]$^{2-}$ with **1a** and Me$_3$SiCl gave a mixture of nonchelated carbene **5**, trinuclear, ferrocene-bridged (*μ*-1*κC*^{1}:2*κP*) complex **6**, and the expected side product, [W(CO)$_5$(**1a**-*κP*)] (**4**) (Scheme 3). To convert **5**, which is an apparent precursor of a P-chelated carbene, into a complex analogous to **2a**, the mixture of **5** and **6** was heated in toluene (80 °C/4 h) and the resulting material separated by chromatography to give (in order of increasing polarity) unchanged **6**, P-chelated carbene **7**, and [W(CO)$_5$(Ph$_2$PfcCHO-*κP*)] (**8**) as a decomposition product.[17] All compounds were isolated in pure form and characterized except for **5**, which could not be separated from **6** due to similar retention properties; the spectral data for **5** were obtained by subtracting the signals due to **6** from the spectra of the **5**/**6** mixture. The structures of **6** and **7** were determined by single-crystal X-ray diffraction (see below).

Compounds **5**−**8** are easily distinguishable by NMR spectroscopy. Similar to the case for the chromium analogues, the conversion of the amide group into a carbene is reflected by a disappearance of the $\nu_{C=O}$ amide signal in the IR spectra and by a typical low-field carbene signal in the ^{13}C NMR spectra at about δ_C ca. 251 for the nonchelated carbenes **5** and **6**, and at δ_C ca. 261 for the P-chelated carbene **7**. The ^{13}C NMR spectra are also indicative of the CO substitution at tungsten: carbene **5** shows two (intensity 1 + 4) ^{183}W-coupled signals, while the trinuclear complex **6** exhibits two such sets, one of which is further split into doublets by the phosphine group. The chelated carbene **7** displays three different phosphorus-coupled CO signals (intensity 1 + 1 + 2). In addition, the carbenes show ^{31}P NMR shifts typical of an uncoordinated (**5**, δ_P −18.2), P-coordinated (**6**, δ_P 11.0), or P-chelating (**7**, δ_P 27.9) ferrocenylphosphino group—with (**6** and **7**) or without (**5**) ^{183}W satellites.

Scheme 4



On the other hand, the phosphine complexes **4** and **8** show ^{13}C NMR signals due to a carbonyl group (amide or aldehyde) and two phosphorus-coupled signals for the tungsten-bonded CO ligands with ^{183}W satellites. These features, as well as the ^{31}P NMR shifts (δ_P; **4**, 11.2; **8**, 11.1), correspond nicely to a complex with a *P*-coordinated Hdpf, [W(CO)$_5$(Hdpf-*κP*)] (cf. δ_P 10.9, $^{1}J_{WP}$ = 247 Hz),[16] and, in the case of **8**, also to IR and NMR spectra of uncoordinated Ph$_2$PfcCHO (CHO: δ_H 9.67, δ_C 193.44; $\nu_{C=O}$ 1677 s, 1662 s).[12c]

Reaction with Iron Carbonylate. The reaction of [Fe(CO)$_4$]$^{2-}$ with **1a** as described above for chromium carbonylate gave the ochre phosphine complex **9** as the only isolated product (Scheme 4; 56% yield). The compound shows typical amide and CO signals in the IR and NMR spectra, and its ^{13}C and ^{31}P NMR parameters correspond with the spectra of the related complexes [Fe(dppf-*κP*)(CO)$_4$] and [(*μ*-dppf){Fe(CO)$_4$}$_2$] (dppf = 1,1′-bis(diphenylphosphino)ferrocene).[18] In addition, the structure of **9** was determined by single-crystal X-ray diffraction (see below). The exclusive formation of **9** is rather surprising, in view of the fact that tertiary aromatic, heterocyclic amides and HC(O)NMe$_2$ react

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[16] Lukešová, L.; Ludvík, J.; Císařová, I.; Štěpnička, P. *Collect. Czech. Chem. Commun.* **2000**, *65*, 1897.

[17] Compound **8** was detected also as a minor impurity in a mixture of **5** and **6** which had been recovered from a CDCl$_3$ solution after NMR measurements and analyzed again after standing for about 1 month at +4 °C in the dark. It is known that aldehydes result from hydrolysis of alkoxycarbenes[17a] and were observed as side products in reactions of aminocarbenes at elevated temperatures.[17b,c] (a) Aumann, R.; Hinterding, P.; Krüger, C.; Goddard, R. *J. Organomet. Chem.* **1993**, *459*, 145. (b) Sierra, M. A.; del Amo, J. C.; Mancheo, M. J.; Gómez-Gallego, M. *J. Am. Chem. Soc.* **2001**, *123*, 851. (c) Woodgate, P. D.; Sutherland, H. S.; Rickard, C. E. F. *J. Organomet. Chem.* **2001**, *627*, 206.

[18] (a) Kim, T.-J.; Kwon, K.-H.; Kwon, S.-C.; Baeg, J.-O.; Lee, D.-H. *J. Organomet. Chem.* **1990**, *389*, 205. (b) Kim, T.-J.; Kwon, S.-C.; Kim, Y.-H.; Heo, N. H.; Teeter, M. T.; Yamano, A. *J. Organomet. Chem.* **1991**, *426*, 71.

Table 1. Selected Bond Distances (Å) and Angles (deg) for $\mathbf{2a}\cdot CH_2Cl_2$ (M = Cr) and 7 (M = W)[a]

	$\mathbf{2a}\cdot CH_2Cl_2$	**7**		$\mathbf{2a}\cdot CH_2Cl_2$	**7**
Fe−Cg(1)	1.651(1)	1.650(1)	Fe−Cg(2)	1.6475(9)	1.644(1)
M−P	2.3898(6)	2.5391(9)	M−C(28)	1.860(2)	1.985(4)
P−C(6)	1.813(2)	1.800(3)	C(28)−O(2)	1.150(3)	1.154(5)
P−C(16)	1.834(2)	1.839(3)	M−C(29)	1.884(2)	2.031(3)
P−C(22)	1.838(2)	1.841(3)	C(29)−O(3)	1.154(3)	1.151(4)
M−C(11)	2.148(2)	2.268(4)	M−C(30)	1.891(2)	2.018(4)
C(1)−C(11)	1.499(3)	1.510(5)	C(30)−O(4)	1.147(3)	1.150(5)
C(11)−N	1.326(3)	1.324(4)	M−C(31)	1.857(2)	2.000(4)
N−C(12)	1.495(3)	1.489(4)	C(31)−O(5)	1.153(3)	1.146(5)
N−C(14)	1.478(3)	1.482(4)			
Cp(1)−Cp(2)	3.3(1)	2.1(2)	P−M−C(11)	91.79(6)	90.8(1)
C(1)−C(11)-N	111.2(2)	109.9(3)	C(6)−P−C(16)	103.95(9)	101.9(1)
C(11)−N−C(12)	125.5(2)	126.2(3)	C(6)−P−C(22)	98.43(9)	101.0(1)
C(11)−N−C(14)	123.4(2)	122.8(3)	C(16)−P−C(22)	100.88(9)	101.3(1)

[a] Ring plane definitions: Cp(1), C(1−5); Cp(2), C(6−10). Cg1 and Cg2 are the respective ring centroids.

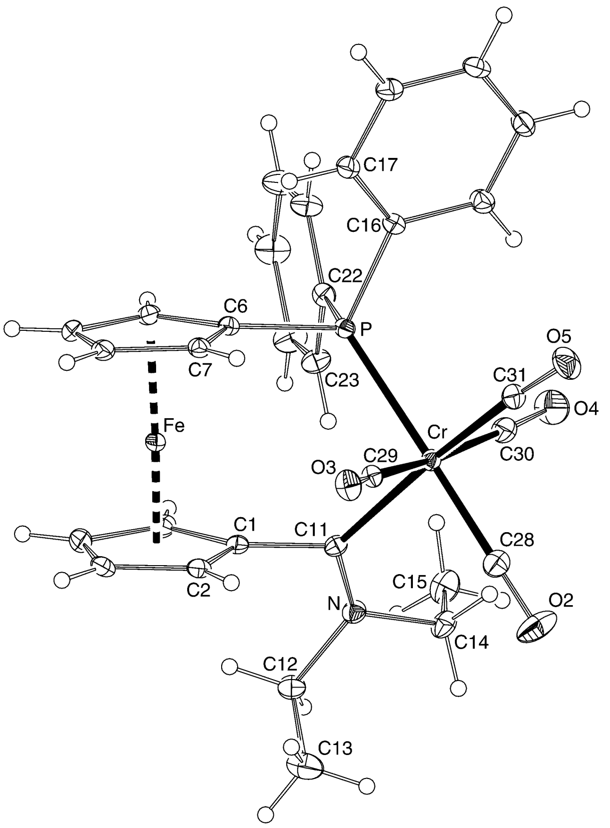

Figure 1. View of the molecular structure of $\mathbf{2a}\cdot CH_2Cl_2$. The solvate molecule is omitted. Thermal motion ellipsoids are drawn at the 30% probability level.

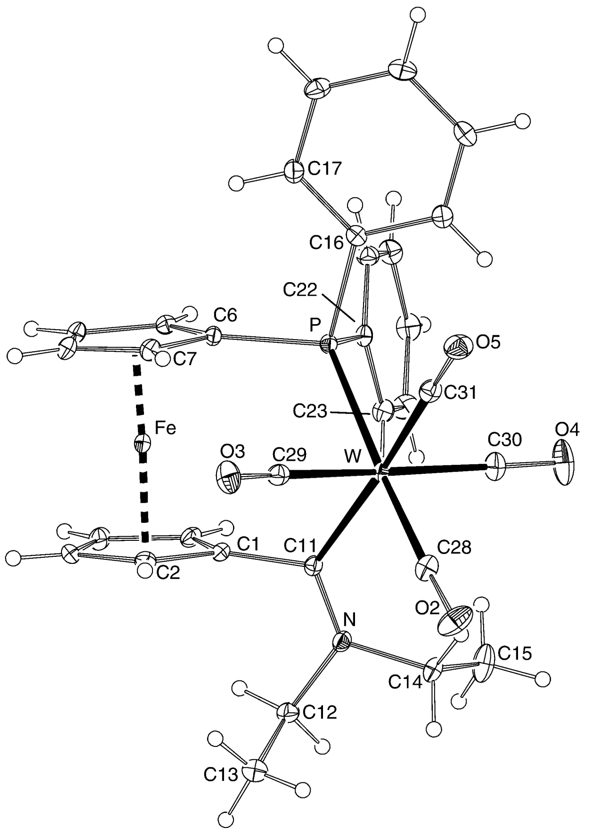

Figure 2. View of the molecular structure of **7**. Thermal motion ellipsoids are drawn at the 30% probability level.

smoothly with $[Fe(CO)_4]^{2-}$ under identical conditions, affording the respective iron aminocarbenes.[19]

Structure Determination. Carbenes 2 and 7. The overall structures of the chelated carbenes $\mathbf{2a}\cdot CH_2Cl_2$ (Figure 1, Table 1), **7** (Figure 2, Table 1), and **2b** (Figure 3, Table 2) are similar and, hence, will be discussed jointly. The bite angles of the (phosphinoferrocenyl)methylidene ligand (P−M−C11) as well as other interligand angles in carbenes **2** and **7** do not differ much from the octahedral values. The coordination spheres are thus asymmetric only in the metal−donor distances, which themselves are unexceptional when compared to those of similar compounds. For instance, the Cr−P distances are similar to those of $[Cr(CO)_5(Hdpf\text{-}\kappa P)]$ (Cr−P = 2.413(6) Å),[16] $[(\mu\text{-dppf})\{Cr(CO)_5\}_2]$ (Cr−P = 2.389(2) Å),[20] and *trans*-$[PtCl_2\{(\mu\text{-dppf})(Cr(CO)_5)\}_2]$ (Cr−P = 2.546(2) Å),[21] while the distances in **7** compare favorably to those in its methoxy analogue **II** (M = W;[8,22] (W=C = 2.20 Å, W−P = 2.55 Å). In all cases, the lower trans influence of phosphine and carbene donors is reflected by a slight shortening of the M−CO bonds trans to these ligands (relatively by ca. 2%),[23] while all the MC−O bond lengths remain virtually identical.

The ferrocene unit in carbenes **2a**, **2b**, and **7** remains essentially undisturbed, showing a maximum cyclo-

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Table 2. Selected Bond Distances (Å) and Angles (deg) for 2b[a]

Fe−Cg(1)	1.6448(8)	Fe−Cg(2)	1.6391(8)
Cr−P	2.4092(6)	Cr−C(28)	1.848(2)
P−C(6)	1.809(2)	C(28)−O(2)	1.157(2)
P−C(16)	1.833(2)	Cr−C(29)	1.890(2)
P−C(22)	1.842(2)	C(29)−O(3)	1.155(2)
Cr−C(11)	2.139(2)	Cr−C(30)	1.888(2)
C(1)−C(11)	1.500(2)	C(30)−O(4)	1.151(2)
C(11)−N	1.325(2)	Cr−C(31)	1.854(2)
N−C(12)	1.475(2)	C(31)−O(5)	1.155(2)
N−C(15)	1.491(2)	C(12)−C(13)	1.515(3)
O(1)−C(13)	1.428(2)	C(14)−C(15)	1.515(3)
O(1)−C(14)	1.424(2)		
Cp(1)−Cp(2)	2.1(1)	C(11)−N−C(12)	124.6(2)
P−Cr−C(11)	90.15(5)	C(11)−N−C(15)	127.4(2)
C(6)−P−C(16)	103.97(8)	C(12)−N−C(15)	109.0(1)
C(6)−P−C(22)	100.75(8)	N−C(12)−C(13)	109.5(2)
C(16)−P−C(22)	99.50(8)	N−C(15)−C(14)	108.8(2)
C(1)−C(11)−N	111.0(1)	C(13)−O(1)−C(14)	110.1(1)

[a] Definitions of the ring planes: Cp(1), C(1−5); Cp(2), C(6−10). Cg(1) and Cg(2) are the respective ring centroids.

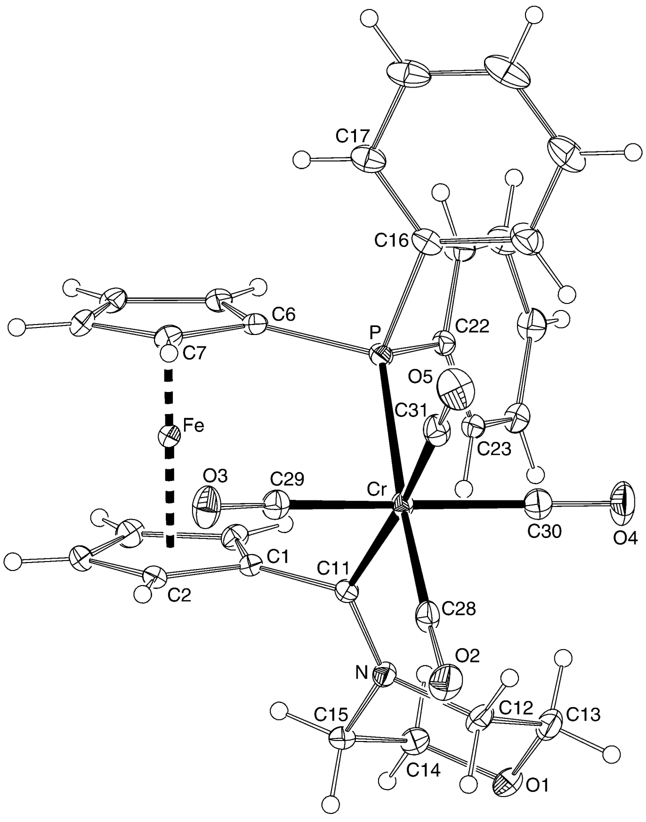

Figure 3. View of the molecular structure of **2b**. Thermal motion ellipsoids are drawn at the 30% probability level.

pentadienyl ring tilt of 3.3(1)° for **2a**. The geometries of the phosphine groups compare well to those of complexes with P-bonded Hdpf,[11a−e] and the C1−C11 distances are identical with that in **9**, where the amide group remains intact. However, the substituents at the ferrocene unit in the carbenes are disposed from the planes of their parent cyclopentadienyl rings, in the same fashion for all the compounds: the phosphorus atoms are inclined toward the iron (distances (Å) from the parent cyclopentadienyl plane: **2a**, 0.216(1); **2b**, 0.286(1); **7**. 0.187(1)) while C1−C11 is bent outward the ferrocene unit (distances (Å) for C11: **2a**, 0.124(2); **2b**, 0.169(2); **7**, 0.161(2)). Hence, the C1−C11 and C(6)−P bonds are tilted from the planes of their cyclopentadienyl rings in the *same* direction. In addition, the ferrocene cyclopentadienyls are rotated from a synclinal eclipsed conformation ($\tau = 5.9(2)$° (**2a**), 10.9(2)° (**2b**), and 12.6(3)°; τ is the torsion angle C1−Cg1−Cg2−C6, see Tables 1 and 2 for definitions), bringing the metal-ligating groups into a position which may further relax the possible steric strain.

6·CHCl₃. The structure of complex **6** (Figure 4, Table 3) combines "independent" phosphine- and carbene-substituted $W(CO)_5$ groups. Similarly to the above cases, the M−CO bonds trans to the phosphine and carbene in both $W(CO)_5$ units are slightly shorter than the other ones and the asymmetry is relayed further to the MC−O bonds, which are longer in trans positions. The W=C (2.284(4) Å) and W−P (2.545(1) Å) distances differ only insignificantly from **7**, further confirming the non-strained nature of carbene **7**. However, a comparison of the structure of **6** with those of P-chelated carbenes **2** and **7** reveals some differences in the geometry of the ferrocene framework: complex **6** shows a notably higher tilt of the cyclopentadienyl rings (9.2(2)°) and the conformation of the ferrocene unit, which is devoid of the geometric constraints imposed by cis chelation, is more opened ($\tau = 88.3(4)$°) to a position almost exactly halfway between synclinal eclipsed ($\tau = 72$°) and anticlinal staggered ($\tau = 108$°).

Complex 9. The molecular structure of **9**, along with selected geometric parameters, is shown in Figure 5. The complex possesses a trigonal-bipyramidal structure with the phosphine ligand attached in an axial position. The coordination geometry at Fe2 is unsymmetric in the Fe2−donor distances (Fe2−P vs four shorter, almost identical Fe2−CO bonds) but displays the regular interligand angles, not differing much from those in the related complexes $[Fe(dppf\text{-}\kappa P)(CO)_4]$ and $[(\mu\text{-}dppf\text{-}1\kappa P{:}2\kappa P')\{Fe(CO)_4\}_2]$.[18b] The ferrocene unit adopts a conformation between anticlinal staggered and anticlinal eclipsed, although closer to the latter ($\tau = 132.7(2)$°), and shows a negligible tilt of the cyclopentadienyl rings (4.3(1)°). Its amide substituent remains untouched by coordination of the phosphino part, showing a geometry typical for simple organic amides,[24] but slightly rotated from the plane of its parent cyclopentadienyl ring (dihedral angle 20.3(2)°).

Electrochemistry. The amides **1** and the series of chromium complexes **2** and **3** were studied by cyclic voltammetry on a stationary platinum-disk electrode and by voltammetry on the rotating platinum-disk electrode (Pt-RDE) in dichloromethane. The amides exhibit one-electron reversible oxidation waves at similar potentials due to the ferrocene backbone (Table 4). The potentials are approximately 100 mV more negative than that of Hdpf ($E° = 0.32$ V vs ferrocene/ferrocenium),[15,10] indicating an easier oxidation of **1**, which is in accordance with a lower electron-withdrawing ability ($-I$) and a higher $+M$ effect of an amino group as compared to that of a hydroxy group.[25] The redox response of the phosphine complexes **3** is also rather straightforward: the complexes undergo two one-electron, reversible oxidations. The first one, around 0.30 V, can be attributed to the ferrocene unit (ferrocene/

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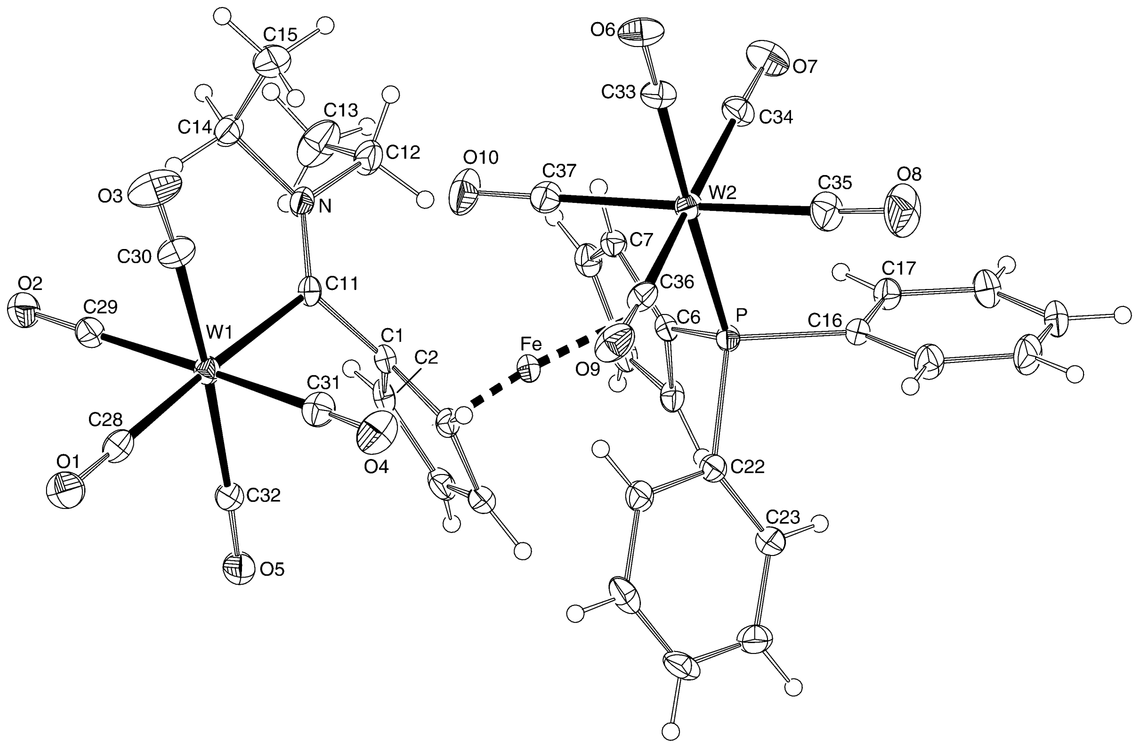

Figure 4. View of the molecular structure of **6**·$CHCl_3$. Thermal motion ellipsoids are drawn at the 30% probability level. The solvent molecule is not shown.

Table 3. Selected Bond Distances (Å) and Angles (deg) for 6·$CHCl_3$[a]

Fe−Cg(1)	1.673(2)	Fe−Cg(2)	1.663(2)
W(1)−C(11)	2.284(4)	W(2)−P	2.545(1)
C(1)−C(11)	1.501(5)	P−C(6)	1.809(4)
C(11)−N	1.313(5)	P−C(16)	1.835(4)
N−C(12)	1.480(6)	P−C(22)	1.830(4)
N−C(14)	1.479(5)		
W(1)−C(28)	1.987(5)	W(2)−C(33)	1.997(4)
C(28)−O(1)	1.169(6)	C(33)−O(6)	1.146(5)
W(1)−C(29)	2.045(4)	W(2)−C(34)	2.059(4)
C(29)−O(2)	1.132(5)	C(34)−O(7)	1.131(6)
W(1)−C(30)	2.028(5)	W(2)−C(35)	2.038(5)
C(30)−O(3)	1.142(6)	C(35)−O(8)	1.136(6)
W(1)−C(31)	2.052(4)	W(2)−C(36)	2.038(4)
C(31)−O(4)	1.140(6)	C(36)−O(9)	1.136(5)
W(1)−C(32)	2.070(4)	W(2)−C(37)	2.037(4)
C(32)−O(5)	1.132(5)	C(37)−O(10)	1.139(6)
Cp(1)−Cp(2)	9.2(2)	C(6)−P−C(16)	101.9(2)
C(1)−C(11)-N	118.5(3)	C(6)−P−C(22)	103.0(2)
C(11)−N−C(12)	125.6(3)	C(16)−P−C(22)	102.3(2)
C(11)−N−C(14)	122.4(3)		

[a] Definitions of the ring planes: Cp(1), C(1−5); Cp(2), C(6−10). Cg(1) and Cg(2) are the corresponding ring centroids.

ferrocenium). This potential is more positive than for **1**, due to a lowered electron density at the ferrocene unit resulting from coordination of **1** to chromium (the differences of the first redox potentials for **3** and **1** are similar: $E°(\mathbf{3b}) - E°(\mathbf{3a}) = 30$ mV, $E°(\mathbf{1b}) - E°(\mathbf{1a}) = 20$ mV). The second oxidation at 0.88 V is chromium-centered, which is supported by a comparison with $[Cr(CO)_5(Hdpf\text{-}\kappa P)]$,[16] where the first wave is shifted more positively (0.50 V) due to the mentioned substituent effects, whereas the second oxidation occurs at a similar potential (+0.85 V).

The redox behavior of **2** cannot be interpreted as simply as that of **1** and **3**. It has been shown that carbenes $[FcC(Y){=}Cr(CO)_5]$ display a single, one-electron wave, whose position changes with Y ($E° = 0.30$ V (Y = OMe), 0.31 V (OEt), and 0.12 V (pyrrolidin-4-yl) in CH_2Cl_2). This oxidation has been ascribed to removing an electron from a molecular orbital which encompasses both metal centers.[26] On the other hand, the carbenes *all-trans*-$Fc(CH{=}CH)_nC(OMe){=}Cr(CO)_5$ ($n = 1-3$) show two successive one-electron waves, assigned by spectroelectrochemical measurements to oxidations of separate (but electronically communicating) ferrocene and carbene units.[5a]

The carbenes **2** exhibit two one-electron redox processes; the first oxidation is reversible, shifted to markedly lower potentials than in other compounds mentioned in this study ($E° < 0$ V). The second step occurs approximately 350 mV more positive. This remarkable negative shift of the first oxidation wave in **2** can be accounted for by a cooperative influence of the higher electron-donating ability of NR_2 as compared to the OR group (see $E°$ values for the $[FcC(Y){=}Cr(CO)_5]$ series above) and an electron density increase resulting from a replacement of one CO ligand with a phosphine, which makes the oxidation easier (cf. $E°$ in $[CrL(CO)_5]$:[25b] L = CO, $E° > 1.2$ V; L = PPh_3, $E° = 0.76$ V). The latter assumption is further supported by an observed $pK_a(CH_3)$ increase by nearly two orders of magnitude upon replacement of one carbonyl ligand in the methylcarbene species $[(OC)_5Cr{=}C(\mathit{Me})OMe]$ with PPh_3, which points to a higher electron density at chromium and, consequently, at the methyl group.[27]

The question of whether the two oxidation steps observed for **2** can be assigned to isolated molecular

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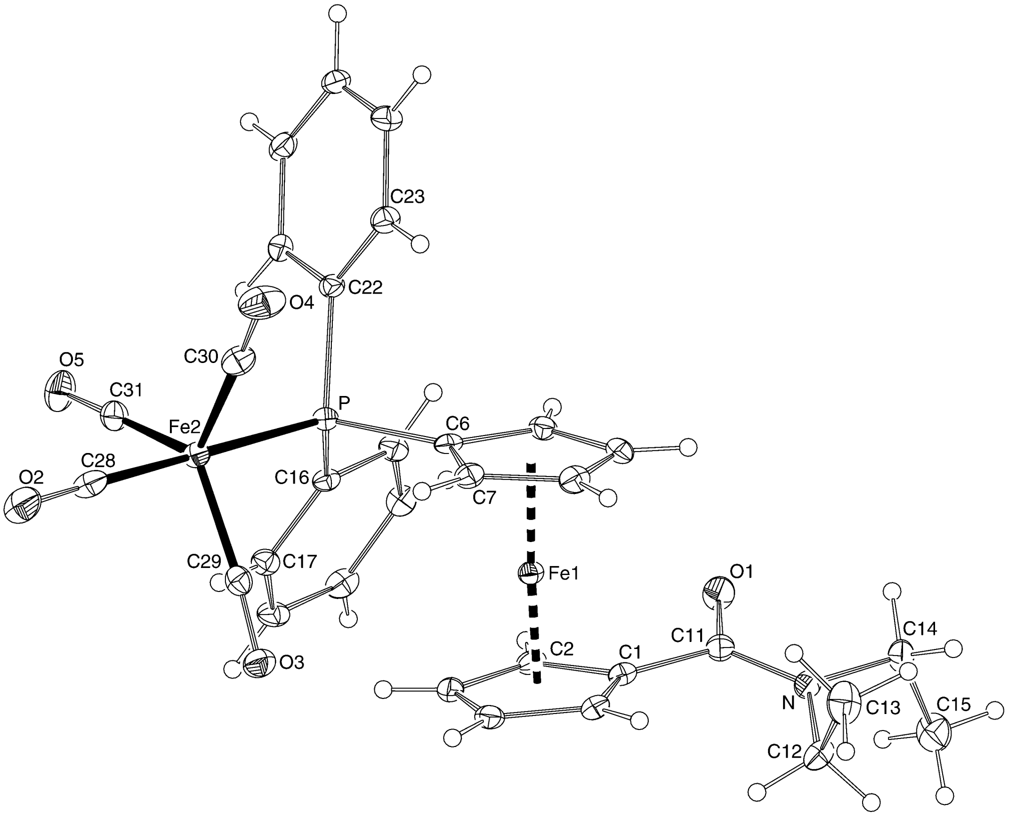

Figure 5. View of the molecular structure of **9** drawn at the 30% probability level. Selected interatomic distances (Å) and angles (deg): Fe(2)−P = 2.2505(6), Fe(2)−C(28) = 1.790(2), C(28)−O(2) = 1.144(3), Fe(2)−C(29) = 1.787(2), C(29)−O(3) = 1.155(2), Fe(2)−C(30) = 1.800(2), C(30)−O(4) = 1.143(3), Fe(2)−C(31) = 1.794(2), C(31)−O(5) = 1.147(3), P−C(6) = 1.808(2), P−C(16) = 1.830(2), P−C(22) = 1.829(2), C(1)−C(11) = 1.498(2), N−C(11) = 1.356(2), C(11)−O(1) = 1.236(2), N−C(12) = 1.464(3), C(12)−C(13) = 1.520(3), N−C(14) = 1.465(2), C(14)−C(15) = 1.524(3); P−Fe(2)−C(28) = 177.29(8), P−Fe(2)−C(29,30,31) = 87.77(6)−92.08(6), C−P−C = 102.76(8)−104.31(8), N−C(11)−O(1) = 121.0(2), C(1)−C(11)−O(1) = 118.1(2), C(1)−C(11)−N = 120.9(2), C(12)−N−C(14) = 115.3(2), C(11)−N−C(12) = 126.1(2), C(11)−N−C(14) = 118.6(2).

Table 4. Electrochemical Data for Chromium Complexes 1−3[a]

	first wave			second wave		
compd	$E°$ (V)	ΔE_p (mV)	$E_{1/2}$ (V)	$E°$ (V)	ΔE_p (mV)	$E_{1/2}$ (V)
1a	0.20	75	0.20			
1b	0.22	85	0.22			
2a	−0.13	60	−0.13	0.23	80	*b*
2b	−0.08	70	−0.07	0.27	120	*b*
3a	0.33	90	0.33	0.88	100	0.88
3b	0.36	80	0.36	0.88	100	0.89

[a] The potentials are given relative to internal ferrocene/ferrocenium. $E°$ is the redox potential from cyclic voltammetry, defined as $E° = {}^1/_2(E_{pa} + E_{pc})$, while ΔE_p denotes the separation of the cyclic voltammetric peaks: $\Delta E_p = E_{p,a} - E_{p,c}$. $E_{p,a}$ and $E_{p,c}$ are the anodic and cathodic peak potentials, respectively. $E_{1/2}$ is the half-wave potential, determined by voltammetry. [b] Not read; the voltammetric wave is tilted.

parts or are two successive oxidations of the whole molecular system remains unaddressed. The latter alternative seems to be more likely, considering the conjugated nature of these compounds and rather large separations of the metal center (**2a**, 4.0828(4) Å; **4b**, 4.0876(4) Å; **7**, 4.1945(4) Å; cf. Fe−W1 = 5.2323(6) Å and Fe−W2 = 5.0188(6) Å for **5**), which rule out direct metal−metal bonding but not an electrostatic interaction.

Conclusion

Phosphinoamides **1** are valuable building blocks for organometallic synthesis, allowing access to unique chromium carbene complexes **2** with P-chelating phosphinoferrocenyl substituents. Formation of carbenes **2** from the amides and $[Cr(CO)_5]^{2-}$ salts evenly competes with the formation of phosphine complexes **3**; both products can be separated from the reaction mixtures by chromatography. The parallel formation of the phosphine complexes from *possibly* unreacted $[Cr(CO)_6]$ in the efficiently formed carbonylate salt is very unlikely, since a replacement of one carbonyl ligand in the carbonyl with Hdpf, the acid parent to the amides **1**, does not proceed willingly (the substitution can be effected using the labile intermediate $[Cr(CO)_5(THF)]$).[16]

A similar synthesis of the tungsten analogues is much less satisfactory, due to a more complicated reaction sequence and lower yields, and not feasible at all for the reaction of $[Fe(CO)_4]^{2-}$ with **1a**, since the side reaction prevails, giving the phosphine carbonyl complex **9** as the only isolated product.

P-chelated carbenes **2** are most likely formed in a stepwise manner by a sequence of the carbene-forming reaction and a subsequent intramolecular substitution of one CO ligand, as suggested for the alkoxy analogues **II**.[8] Strong support for this mechanism comes from the reactions of kinetically more stable tungsten analogues, where the anticipated intermediate, the simple carbene **5**, was characterized and further converted to **7**. Formation of the chelated carbenes from nonchelated precursors cannot be simply reversed; carbenes **2** and **7** do not react in solution with CO gas (1 atm). As indicated by electrochemical measurements, carbenes **2** are an example of the cooperative effect of the metal center enhanced by a conjugated bridge.

Experimental Section

Chemicals and Methods. All syntheses were carried out under argon with the exclusion of direct sunlight. Dichloromethane used in the syntheses was dried over potassium carbonate. THF and toluene were freshly distilled from sodium−benzophenone ketyl. Diethylamine and morpholine were distilled from sodium under argon. Other chemicals were prepared by the literature procedures (see below) or used as received from commercial suppliers.

NMR spectra were recorded on a Varian UNITY Inova 400 spectrometer at 399.95 (^{1}H), 100.58 (^{13}C), and 161.90 MHz (^{31}P). Chemical shifts (δ/ppm) are referenced to internal tetramethylsilane (^{1}H, ^{13}C) and external 85% aqueous H_3PO_4 (^{31}P). IR spectra were recorded on either a Nicolet 740 or a Nicolet Magna FT IR spectrometer. Mass spectra were measured using an Autospec Ultima or a ZAB-SEQ VG analytical spectrometer operating in positive-ion electron impact (EI) or fast atom bombardment (FAB) modes.

Electrochemical measurements were carried out with a multipurpose PA3 polarograph interfaced to a Model 4103 XY recorder (Laboratorní přístroje, Prague, Czech Republic) at room temperature using a standard three-electrode system: platinum-disk working electrode, platinum-wire auxiliary electrode, and Ag/AgCl (1 M KCl) reference electrode. The analyzed solutions contained a ca. 4×10^{-4} M concentration of the analyte and 0.1 M Bu_4NPF_6 (Fluka, purissimum for electrochemistry) as the supporting electrolyte in dichloromethane (Merck p.a., used without further purification). Prior to the measurement, the solutions were purged with argon and kept under an argon blanket. Cyclic voltammograms were recorded on a stationary disk electrode (scan rate 100 mV s^{-1}), while the voltammograms were measured with a rotating electrode (1000 min^{-1}, scan rate 20 mV s^{-1}). The potentials are given in volts relative to the redox potential of the ferrocene/ferrocenium standard.

Preparation of Amides 1. *N,N*-Diethyl-1′-(diphenylphosphino)ferrocenecarboxamide (1a). To an ice-cooled solution of Hdpf[10] (2.072 g, 5.00 mmol) in dry dichloromethane (75 mL) was added 1-hydroxybenzotriazole (0.748 g, 5.5 mmol) and *N*-(3-(dimethylamino)propyl)-*N*′-ethylcarbodiimide (0.861 g, 5.5 mmol). The mixture was stirred at 0 °C for 1 h; the triazole quickly dissolved. Neat diethylamine (0.64 mL, 6.2 mmol) was added, the cooling bath was removed, and stirring was continued at room temperature overnight. The reaction mixture was extracted with 3 M HCl, saturated aqueous $NaHCO_3$, and water, and the organic phase was dried ($MgSO_4$) and evaporated. The residue was purified by flash chromatography on silica gel using dichloromethane−methanol (10:1) as the eluent. Evaporation (at 60 °C/0.3 Torr for 30 min) yielded a red-orange oil which solidified upon standing at room temperature to give a rusty brown amorphous solid. Yield: 2.141 g (91%).

^{1}H NMR ($CDCl_3$): δ 1.16 (t, $^{3}J_{HH} = 7.1$ Hz, 6 H, *Me*); 3.44 (br q, $^{3}J_{HH} \approx 7$ Hz, 4 H, NC*H*$_2$); 4.15 (apparent q, 2 H, C*H*, fc); 4.18, 4.46, 4.51 (3 × apparent t, 2 H, C*H*, fc); 7.28−7.39 (m, 10 H, P*Ph*$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 0.13.7 (br, *Me*); ∼41.7 (br, N*C*H$_2$); 70.89, 71.09, 73.74 (br d, $J_{PC} \approx 4$ Hz), 74.11 (d, $J_{PC} = 14$ Hz) (4 × *C*H, fc); 79.71 (*C*$_{ipso}$, fc); 128.20 (d, $J_{PC} = 7$ Hz), 128.70, 133.43 (d, $J_{PC} = 19$ Hz) (3 × *C*H, PPh$_2$); ∼133.8 (br, *C*$_{ipso}$, PPh$_2$); 169.05 (*C*═O); the second *C*$_{ipso}$(fc) resonance is probably obscured by the solvent signal. ^{31}P{^{1}H} NMR ($CDCl_3$): δ −16.8 (s). IR (Nujol): ν/cm^{-1} $\nu_{C=O}$ 1629 (vs), 1620 (vs). HR MS (EI): calcd for $C_{27}H_{28}{}^{56}FeNOP$ (M^+), 469.1258; found, 469.1276. Anal. Calcd for $C_{27}H_{28}FeNOP$: C, 69.10; H, 6.01; N, 2.98. Found: C, 69.01; H, 6.23; N, 3.10.

Morpholide 1b. Amide **1b** was obtained by a similar protocol, starting with Hdpf[10] (1.243 g, 3.00 mmol), 1-hydroxybenzotriazole (0.446 g, 3.3 mmol), *N*-(3-(dimethylamino)propyl)-*N*′-ethylcarbodiimide (0.512 g, 3.3 mmol), and morpholine (0.30 mL, 3.44 mmol) in dichloromethane (50 mL). Yield: 1.434 g (99%) of an orange-red oil which solidifies upon standing.

^{1}H NMR ($CDCl_3$): δ 3.60−3.68 (m, 8 H, NC*H*$_2$C*H*$_2$O); 4.15 (apparent q, 2 H, C*H*, fc); 4.21, 4.36, 4.49 (3 × apparent t, 2 H, C*H*, fc); 7.29−7.38 (m, 10 H, P*Ph*$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ ∼45 (very br, N*C*H$_2$); 66.93 (O*C*H$_2$); 70.73, 71.17, 73.56 (d, $J_{PC} = 4$ Hz), 74.31 (d, $J_{PC} = 14$ Hz) (4 × *C*H, fc); 79.00 (*C*$_{ipso}$, fc); 128.21 (d, $J_{PC} = 7$ Hz), 128.65, 133.44 (d, $J_{PC} = 19$ Hz) (3 × *C*H, PPh$_2$); 133.49 (d, $^{1}J_{PC} = 9$ Hz, *C*$_{ipso}$, PPh$_2$); 169.12 (*C*═O); the other *C*$_{ipso}$(fc) was not found. ^{31}P{^{1}H} NMR ($CDCl_3$): δ −16.9 (s). IR (Nujol): ν/cm^{-1} $\nu_{C=O}$ 1612 (vs), 1605 (vs). HR MS (EI): calcd for $C_{27}H_{26}{}^{56}FeNO_2P$ (M^+), 483.1051; found, 483.1002.

Synthesis of [(Diethylamino){1′-(diphenylphosphino-κ*P*)ferrocenyl}methylidene-κ*C*^{1}]tetracarbonylchromium(0) (2a) and [*N,N*-Diethyl-1′-(diphenylphosphino-κ*P*)ferrocenecarboxamide]pentacarbonylchromium(0) (3a). A solution of sodium naphthalenide, prepared by stirring sodium metal (48 mg, 2.1 mmol) and naphthalene (272 mg, 2.1 mmol) in anhydrous THF (5 mL) at room temperature until all the metal dissolved, was added at −78 °C via a syringe into a solution of chromium hexacarbonyl (176 mg, 0.8 mmol) in the same solvent (5 mL). The reaction mixture was warmed to 0 °C, stirred for 30 min, and cooled to −78 °C. Amide **1a** (328 mg, 0.7 mmol) in THF (2 mL) was added to the solution of carbonylate salt $Na_2[Cr(CO)_5]$, and the mixture was warmed to 0 °C and stirred at this temperature for 30 min. Then, it was recooled to −78 °C and treated with trimethylchlorosilane (0.2 mL, 1.6 mmol). After the mixture was stirred at −78 °C for another 30 min, the cooling bath was removed and the reaction mixture was brought to room temperature for 1 h with stirring and mixed with neutral alumina (1 g). The solvent was removed under vacuum and the residue carefully dried under vacuum of an oil pump to remove all volatiles. The solid residue was mixed with light petroleum (2 mL) and the suspension transferred to a chromatographic column filled with neutral alumina (15 g). Naphthalene was removed with hexane. A subsequent successive elution with hexane−dichloromethane (1:1) and dichloromethane afforded respectively carbene **2a** (bright orange solid; 200 mg, 46%) and the phosphine complex **3a** (orange waxy solid; 172 mg, 37%).

Analytical data for **2a** are as follows. ^{1}H NMR ($CDCl_3$): δ 1.00, 1.61 (2 × t, $^{3}J_{HH} = 7.2$ Hz, 3 H, *Me*); 3.45 (q, $^{3}J_{HH} = 7.2$ Hz, 2 H, NC*H*$_2$); 4.14 (apparent t, 2 H), 4.18 (br s, 2 H), 4.35 (br apparent t, 2 H), 4.41 (br s, 2 H) (4 × C*H*, fc); 4.84 (q, $^{3}J_{HH} = 7.2$ Hz, 2 H, NC*H*$_2$); 7.31−4.78 (m, 10 H, P*Ph*$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 13.98, 14.26 (*Me*); 46.67, 56.91 (N*C*H$_2$); 67.48, 67.83 (br), 71.63 (br d, $J_{PC} \approx 5$ Hz), 76.88 (d, $J_{PC} = 10$ Hz) (4 × *C*H, fc); 84.13 (d, $^{1}J_{PC} = 34$ Hz, *C*P, fc); 109.24 (d, $^{3}J_{PC} = 5$ Hz, *C*C═Cr, fc); 127.73 (d, $J_{PC} = 9$ Hz), 129.37 (d, $J_{PC} \approx 1$ Hz), 133.17 (d, $J_{PC} = 11$ Hz) (3 × *C*H, PPh$_2$); 137.90 (d, $^{1}J_{PC} = 32$ Hz, *C*$_{ipso}$, PPh$_2$); 221.63 (d, $^{2}J_{PC} = 15$ Hz), 227.33 (d, $^{2}J_{PC} = 10$ Hz), 227.89 (3 × *C*≡O); 279.21 (d, $^{2}J_{PC} = 13$ Hz, *C*═Cr). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 58.1 (s). IR ($CHCl_3$): ν/cm^{-1} $\nu_{C\equiv O}$ 1993 vs, 1897 s, 1871 br vs. MS (EI): *m*/*z* 589 ($[M - CO]^+$), 505 ($[M - 4\,CO]^+$), 476 ($[M - CO - C_2H_5]^+$), 434 ($[M - 4\,CO - NC_4H_9]^+$). Anal. Calcd for $C_{31}H_{28}CrFeNO_4P\cdot{}^{2}/_{3}CH_2Cl_2$: C, 56.43; H, 4.39; N, 2.08. Found: C, 56.42; H, 4.54; N, 1.91 (the complex tends to retain solvent in the structure upon recrystallization from dichloromethane; the solvent content was verified by ^{1}H NMR).

Analytical data for **3a** are as follows. ^{1}H NMR ($CDCl_3$): δ 1.11 (br s, 6 H, *Me*); 3.35 (br s, 4 H, C*H*$_2$); 4.03 (apparent t, 2 H), 4.34 (apparent t, 2 H), 4.36 (apparent q, 2 H), 4.60 (br apparent t, 2 H) (4 × C*H*, fc); 7.39−7.50 (m, 10 H, P*Ph*$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 12.79, 14.63 (br, *Me*); 40.65, 42.65 (*C*H$_2$); 71.11, 71.13, 74.67 (d, $J_{PC} = 11$ Hz), 74.90 (d, $J_{PC} = 11$

Hz) (4 × *C*H, fc); 79.89 (d, $^{1}J_{\mathrm{PC}} = 39$ Hz, *C*P, fc); 81.32 (*C*−CO, fc); 128.15 (d, $J_{\mathrm{PC}} = 9$ Hz), 128.94 (d, $J_{\mathrm{PC}} = 2$ Hz), 132.28 (d, $J_{\mathrm{PC}} = 11$ Hz) (3 × *C*H, PPh$_2$); 137.82 (d, $^{1}J_{\mathrm{PC}} = 39$ Hz, C_{ipso}, PPh$_2$), 168.37 (*C*=O), 216.74 (d, $^{2}J_{\mathrm{PC}} = 13$ Hz), 221.28 (d, $^{2}J_{\mathrm{PC}} = 7$ Hz) (2 × *C*≡O). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 47.3 (s). IR (CHCl$_3$): ν/cm^{-1} $\nu_{\mathrm{C\equiv O}}$ 2063 s, 1984 m, 1939 br vs; $\nu_{\mathrm{C=O}}$ 1614 m. MS (EI): *m*/*z* 661 (*M*$^+$), 521 ([*M* − 5 CO]$^+$), 469 ([Ph$_2$PfcC(O)NEt$_2$]$^+$). HR MS (EI): calcd for $C_{27}H_{28}{}^{52}Cr^{56}FeNOP$ ([*M* − 5 CO]$^+$), 521.0663; found, 521.0657.

Synthesis of [(4-Morpholinyl){1′-(diphenylphosphino-κ*P*)ferrocenyl}methylidene-κ*C*^{1}]-tetracarbonylchromium(0) (2b) and [1′-(Diphenylphosphino-κ*P*)ferrocenecarboxylic acid morpholide]pentacarbonylchromium(0) (3b). With morpholide **1b** as starting material (338 mg, 0.7 mmol), the same procedure as above afforded a mixture of morpholide complexes **2b** and **3b**. Chromatography on alumina with hexane−dichloromethane (1:1) as the eluent gave a small amount of colored byproducts, immediately followed by **2b** (bright orange solid; 85 mg, 19%). Further elution with dichloromethane yielded **3b** as an orange solid (182 mg, 38%).

Analytical data for **2b** are as follows. ^{1}H NMR (CDCl$_3$): δ 3.48 (m, 2 H, C*H*$_2$); 3.64 (m, 2 H, C*H*$_2$); 4.13 (br s, 2 H, C*H*, fc); 4.15−4.19 (m, 4 H, C*H*$_2$ and C*H*(fc)); 4.37, 4.72 (2 × br s, 2 H, C*H*, fc); 4.99 (m, 2 H, C*H*$_2$); 7.33−7.48 (m, 10 H, P*Ph*$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 55.30 (*C*H$_2$); 62.58 (*C*H$_2$); 67.74 (*C*H$_2$); 67.97 (*C*H, fc); 68.33 (*C*H$_2$); 71.85 (br, *C*H, fc); 76.86 (d, $J_{\mathrm{PC}} = 10$ Hz, *C*H, fc); 84.17 (d, $^{1}J_{\mathrm{PC}} = 34$ Hz, *C*P, fc); 108.30 (d, $^{3}J_{\mathrm{PC}} = 5$ Hz, *C*C=Cr, fc); 127.84 (d, $J_{\mathrm{PC}} = 9$ Hz); 129.51 (d, $J_{\mathrm{PC}} \approx 2$ Hz); 133.10 (d, $J_{\mathrm{PC}} = 11$ Hz) (3 × *C*H, PPh$_2$); 137.75 (d, $^{1}J_{\mathrm{PC}} = 32$ Hz, C_{ipso}, PPh$_2$); 221.86 (d, $^{2}J_{\mathrm{PC}} = 15$ Hz), 227.03 (d, $^{2}J_{\mathrm{PC}} = 9$ Hz), 228.15 (3 × *C*≡O); 280.46 (d, $^{2}J_{\mathrm{PC}} = 13$ Hz, *C*=Cr); one *C*H(fc) probably overlapped by the solvent signal. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 58.5 (s). IR (CHCl$_3$): ν/cm^{-1} $\nu_{\mathrm{C\equiv O}}$ 1994 vs, 1939 m, 1900 m, 1873 br vs. MS (EI): *m*/*z* 603 ([*M* − CO]$^+$), 519 ([*M* − 4 CO]$^+$), 434 ([*M* − 4 CO − C$_4$H$_7$NO]$^+$). Anal. Calcd for $C_{32}H_{26}FeNO_6P$: C, 58.97; H, 4.15; N, 2.22. Found: C, 58.50; H, 4.13; N, 2.09.

Analytical data for **3b** are as follows. ^{1}H NMR (CDCl$_3$): δ 3.55, 3.59 (2 × br s, 4 H, C*H*$_2$); 4.02 (apparent t, 2 H); 4.28 (apparent t, 2 H), 4.36 (apparent q, 2 H), 4.64 (dt, $J \approx 0.8$, 1.9 Hz, 2 H) (4 × C*H*, fc); 7.40−7.49 (m, 10 H, P*Ph*$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ ∼43.3, ∼47.0 (v br, *C*H$_2$); 66.79 (*C*H$_2$); 71.24, 71.00, 74.84 (d, $J_{\mathrm{PC}} = 7$ Hz), 74.89 (d, $J_{\mathrm{PC}} = 11$ Hz) (4 × *C*H, fc); 80.45 (d, $^{1}J_{\mathrm{PC}} = 38$ Hz, *C*P, fc); 80.48 (*C*−CO, fc); 128.17 (d, $J_{\mathrm{PC}} = 10$ Hz), 129.86 (d, $J_{\mathrm{PC}} = 2$ Hz), 132.25 (d, $J_{\mathrm{PC}} = 11$ Hz) (3 × *C*H, PPh$_2$); 137.82 (d, $^{1}J_{\mathrm{PC}} = 39$ Hz, C_{ipso}, PPh$_2$), 168.34 (*C*=O), 216.70 (d, $^{2}J_{\mathrm{PC}} = 13$ Hz), 221.19 (d, $^{2}J_{\mathrm{PC}} = 7$ Hz) (2 × *C*≡O). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 47.3 (s). IR (CHCl$_3$): ν/cm^{-1} $\nu_{\mathrm{C\equiv O}}$ 2063 s, 1984 m, 1939 br vs; $\nu_{\mathrm{C=O}}$ 1623 m. MS (EI): *m*/*z* 675 (*M*$^+$), 563 ([*M* − 4 CO]$^+$), 535 ([*M* − 5 CO]$^+$), 483 ([Ph$_2$PfcC(O)N(CH$_2$CH$_2$)O]$^+$). HR MS (EI): calcd for $C_{32}H_{26}{}^{52}Cr^{56}FeNO_7P$ (*M*$^{\bullet+}$), 675.0203; found, 675.0206. HR MS (EI): calcd for $C_{27}H_{26}{}^{52}Cr^{56}FeNO_2P$ ([*M* − 5 CO]$^+$), 535.0456; found, 535.0439.

Preparation of Tungsten Complexes. With tungsten hexacarbonyl (564 mg, 1.6 mmol) and **1a** (656 mg, 1.4 mmol) as starting materials, the above method gave a red-orange solid which was purified by chromatography on alumina. Elution with a hexane−dichloromethane mixture (2:1) gave a mixture of **5** and **6** (bright red solid, 125 mg). A further elution with dichloromethane afforded a well-separated band of [W(CO)$_5${Ph$_2$PfcC(O)NEt$_2$-κ*P*}] (**4**) (orange waxy solid; 585 mg, 53%).

The mixture containing **5** and **6** was dissolved in toluene (125 mg in 1 mL) and the solution heated to 80 °C for 4 h. The solvent was removed under reduced pressure and the residue purified by chromatography on silica gel (50 g). Elution with a hexane−dichloromethane mixture (2:1) afforded unchanged **6** (red foam; 29 mg, 2%), subsequent elution with hexane−dichloromethane (1:1) gave the carbene [W(CO)$_4${Ph$_2$PfcC(NEt)$_2$-κ^2*C*^{1},*P*}] (**7**; bright orange crystals; 46 mg, 4%), and, finally, dichloromethane eluted [W(CO)$_5${Ph$_2$PfcCHO-κ*P*}] (**8**; red-orange oil; 37 mg, 3%).

Analytical data for [*N*,*N*-diethyl-1′-(diphenylphosphino-κ*P*)-ferrocenecarboxamide]pentacarbonyltungsten(0) (**4**) are as follows. ^{1}H NMR (CDCl$_3$): δ 1.10 (br s, 6 H, *Me*); 3.34 (br s, 4 H, C*H*$_2$); 4.06 (apparent t, 2 H), 4.34−4.37 (m, 4 H), 4.63 (d of apparent t, 2 H) (4 × C*H*, fc); 7.39−7.48 (m, 10 H, P*Ph*$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 12.81, 14.62 (br, *Me*); 40.63, 42.62 (*C*H$_2$); 71.01, 71.08, 74.91 (d, $J_{\mathrm{PC}} = 12$ Hz), 75.18 (d, $J_{\mathrm{PC}} = 7$ Hz) (4 × *C*H, fc); 79.31 (d, $^{1}J_{\mathrm{PC}} = 45$ Hz, *C*P, fc), 81.41 (*C*−CO, fc), 128.15 (d, $J_{\mathrm{PC}} = 9$ Hz), 130.00 (d, $J_{\mathrm{PC}} = 2$ Hz), 132.42 (d, $J_{\mathrm{PC}} = 12$ Hz) (3 × *C*H, PPh$_2$); 137.76 (d, $^{1}J_{\mathrm{PC}} = 44$ Hz, C_{ipso}, PPh$_2$), 168.32 (*C*=O), 197.28 (d, $^{2}J_{\mathrm{PC}} = 13$ Hz, ^{183}W satellites, $^{2}J_{\mathrm{WC}} = 126$ Hz), 198.77 (d, $^{2}J_{\mathrm{PC}} = 21$ Hz) (2 × *C*≡O). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 11.2 (s; ^{183}W satellites, $^{1}J_{\mathrm{WP}} = 246$ Hz). IR (CHCl$_3$): ν/cm^{-1} $\nu_{\mathrm{C\equiv O}}$ 2071 s, 1982 m, 1982 vs, 1738 m; $\nu_{\mathrm{C=O}}$ 1613 m. MS (EI): *m*/*z* 793 (*M*$^+$), 709 ([*M* − 3 CO]$^+$), 651 ([*M* − 5 CO]$^+$), 469 ([Ph$_2$PfcC(O)NEt$_2$]$^+$). HR MS (EI): calcd for $C_{29}H_{28}{}^{56}FeNO_3P^{184}W$ ([*M* − 3 CO]$^+$), 709.0666; found, 709.0659.

Analytical data for [(diethylamino){1′-(diphenylphosphino)-ferrocenyl}methylidene-κ*C*^{1}]pentacarbonyltungsten(0) (**5**) are as follows. This compound could not be isolated in pure form. NMR data have been obtained by a subtraction of signals due to **6** from the spectra of the above mixture of **5** and **6**. ^{1}H NMR (CDCl$_3$): δ 1.34, 1.41 (2 × t, $^{3}J_{\mathrm{HH}} = 7.2$ Hz, 3 H, *Me*); 4.00 (apparent q, 2 H, fc); 4.25 (q, $^{3}J_{\mathrm{HH}} = 7.2$ Hz, 2 H, NC*H*$_2$), 4.29, 4.39, 4.40 (3 × apparent t, 2 H, fc); 4.80 (q, $^{3}J_{\mathrm{HH}} = 7.2$ Hz, 2 H, NC*H*$_2$); 7.31−7.47 (m, 10 H, P*Ph*$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 14.40, 15.29 (*Me*); 45.77, 58.28 (N*C*H$_2$); 70.85, 71.19, 72.47 (d, $J_{\mathrm{PC}} = 3$ Hz), 74.17 (d, $J_{\mathrm{PC}} = 14$ Hz) (4 × *C*H, fc); 78.34 (d, $^{1}J_{\mathrm{PC}} = 8$ Hz, *C*P, fc); 97.69 (*C*C=Cr, fc); 128.30 (d, $J_{\mathrm{PC}} \approx 10$ Hz), 128.76, 133.40 (d, $J_{\mathrm{PC}} = 19$ Hz) (3 × *C*H, PPh$_2$); 138.12 (d, $^{1}J_{\mathrm{PC}} = 10$ Hz, C_{ipso}, PPh$_2$), 198.96 (s with ^{183}W satellites, $^{1}J_{\mathrm{WC}}$. 114 Hz), 204.09 (2 × C=W(*C*O)$_5$), 251.04 (W=*C*). ^{31}P{^{1}H} NMR (CDCl$_3$): δ −18.2 (s). HR MS (FAB): calcd for $C_{30}H_{28}{}^{56}FeNO_3P^{184}W$ ([*M* − 2 CO]$^+$), 721.0666; found, 721.0673.

Analytical data for [(diethylamino){1′-(diphenylphosphino-2κ*P*)-ferrocenyl}methylidene-1κ*C*^{1}]bis[pentacarbonyltungsten(0)] (**6**) are as follows. ^{1}H NMR (CDCl$_3$): δ 1.32, 1.42 (2 × t, $^{3}J_{\mathrm{HH}} = 7.1$ Hz, 3 H, *Me*); 4.19 (s, 4 H, fc); 4.22 (apparent q, 2 H, fc); 4.26 (q, $^{3}J_{\mathrm{HH}} = 7.1$ Hz, 2 H, NC*H*$_2$); 4.54 (apparent dt, 2 H, fc); 4.71 (q, $^{3}J_{\mathrm{HH}} = 7.1$ Hz, 2 H, NC*H*$_2$); 7.38−7.47 (m, 10 H, P*Ph*$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 14.33, 15.22 (*Me*); 45.48, 58.32 (N*C*H$_2$); 71.00, 71.15, 73.77 (d, $J_{\mathrm{PC}} = 7$ Hz), 74.66 (d, $J_{\mathrm{PC}} = 11$ Hz) (4 × *C*H, fc); 80.80 (d, $^{1}J_{\mathrm{PC}} = 43$ Hz, *C*P, fc); 98.37 (*C*C=Cr, fc); 128.30 (d, $J_{\mathrm{PC}} = 10$ Hz), 130.27 (d, $J_{\mathrm{PC}} = 2$ Hz), 132.38 (d, $J_{\mathrm{PC}} = 12$ Hz) (3 × *C*H, PPh$_2$); 137.35 (d, $^{1}J_{\mathrm{PC}} = 44$ Hz, C_{ipso}, PPh$_2$); 197.14 (d, $^{2}J_{\mathrm{PC}} = 7$ Hz with ^{183}W satellites, $^{1}J_{\mathrm{WC}} = 126$ Hz), 198.47 (d, $^{2}J_{\mathrm{PC}} = 21$ Hz) (2 × PW(*C*O)$_5$); 198.82 (s with ^{183}W satellites, $^{1}J_{\mathrm{WC}} = 128$ Hz), 203.88 (s with ^{183}W satellites, $^{1}J_{\mathrm{WC}} = 127$ Hz) (2 × C=W(*C*O)$_5$); 250.86 (s with ^{183}W satellites, $^{1}J_{\mathrm{WC}}$. 90 Hz, W=*C*). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 11.0 (s; ^{183}W satellites, $^{1}J_{\mathrm{WP}} = 247$ Hz). IR (CHCl$_3$): ν/cm^{-1} $\nu_{\mathrm{C\equiv O}}$ 2072 s, 2060 s, 1928 br vs. HR MS (FAB): calcd for $C_{32}H_{28}{}^{56}FeNO_5P^{184}W_2$ ([*M* − 5 CO]$^+$), 961.0074; found, 961.0091.

Analytical data for [(diethylamino){1′-(diphenylphosphino-κ*P*)ferrocenyl}methylidene-κ*C*^{1}]tetracarbonyltungsten(0) (**7**) are as follows. ^{1}H NMR (CDCl$_3$): δ 1.03, 1.55 (2 × t, $^{3}J_{\mathrm{HH}} = 7.2$ Hz, 3 H, *Me*); 3.44 (q, $^{3}J_{\mathrm{HH}} = 7.2$ Hz, 2 H, NC*H*$_2$); 4.18 (br m, 4 H), 4.37 (s, 4 H) (4 × C*H*, fc); 4.70 (q, $^{3}J_{\mathrm{HH}} = 7.2$ Hz, 2 H, NC*H*$_2$); 7.31−7.48 (m, 10 H, P*Ph*$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 13.91, 14.01 (*Me*); 46.54, 59.55 (N*C*H$_2$); 67.46, 67.86 (br), 71.55 (br d, $J_{\mathrm{PC}} \approx 6$ Hz), ca. 76.7 (d, $J_{\mathrm{PC}} \approx 12$ Hz) (4 × *C*H, fc); 84.10 (d, $^{1}J_{\mathrm{PC}} = 42$ Hz, *C*P, fc); 109.50 (d, $^{3}J_{\mathrm{PC}} = 5$ Hz, *C*C=W, fc); 127.80 (d, $J_{\mathrm{PC}} = 9$ Hz), 129.61 (d, $J_{\mathrm{PC}} = 2$ Hz), 133.43 (d, $J_{\mathrm{PC}} = 12$ Hz) (3 × *C*H, PPh$_2$); 137.40 (d, $^{1}J_{\mathrm{PC}} = 38$ Hz, C_{ipso}, PPh$_2$); 204.94 (d, $^{2}J_{\mathrm{PC}} = 7$ Hz), 209.06 (d, $^{2}J_{\mathrm{PC}} = 31$ Hz), 209.86 (d, $^{2}J_{\mathrm{PC}} = 4$ Hz) (3 × *C*≡O); 260.64 (d, $^{2}J_{\mathrm{PC}} = 9$ Hz, *C*=W). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 27.9 (s; ^{183}W satellites, $^{1}J_{\mathrm{WP}} = 249$ Hz). IR (CHCl$_3$): ν/cm^{-1} $\nu_{\mathrm{C\equiv O}}$ 2001 vs, 1894 s, 1872 br vs. MS (EI): *m*/*z* 749 (*M*$^+$), 721 ([*M* − CO]$^+$), 693 ([*M* − 2 CO]$^+$), 665 ([*M* −

Table 5. Crystallographic Data and Data Collection and Stucture Refinement Details for 2a·CH_2Cl_2, 2b, 6·$CHCl_3$, 7, and 9

	2a·CH_2Cl_2	**2b**	**6**·$CHCl_3$	**7**	**9**
formula	$C_{32}H_{28}Cl_2CrFeNO_4P^c$	$C_{31}H_{26}CrFeNO_5P$	$C_{38}H_{29}Cl_3FeNO_{10}PW_2$	$C_{31}H_{28}FeNO_4PW$	$C_{31}H_{28}Fe_2NO_5P$
mol wt	700.27	631.35	1220.49	749.21	637.21
cryst syst	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	Cc (No. 9)[f]	$P2_1/n$ (No. 14)
a (Å)	10.0026(1)	9.1250(1)	13.7968(2)	9.9709(1)	15.0963(2)
b (Å)	16.9132(2)	9.2763(1)	9.1526(1)	19.0932(3)	8.4394(1)
c (Å)	18.5294(2)	17.0026(3)	33.1824(3)	15.1138(3)	23.0502(3)
α (deg)	90	76.4486(8)	90	90	90
β (deg)	98.0621(6)	77.4729(8)	90.5776(7)	92.778(1)	106.5920(5)
γ (deg)	90	82.9206(7)	90	90	90
V (Å^3)	3103.75(6)	1361.85(3)	4189.95(8)	2873.93(8)	2814.40(6)
Z	4	2	4	4	4
D_c (g cm^{-3})	1.499	1.540	1.935	1.732	1.504
μ(Mo Kα) (mm^{-1})	1.079	1.033	6.104[e]	4.596[g]	1.129
total no. of diffrns	13 927	11 540	52 703	21 249	12 434
no. of unique/obsd[a] diffrns	7094/6189	6212/5224	9567/8125	6337/6253	6441/4977
no. of params	390	361	507	354	363
R (obsd diffrns) (%)[b]	3.58	2.93	2.86	1.71	3.27
R, R_w (all data) (%)[b]	4.26, 9.90	3.95, 6.92	6.90, 6.37	3.81, 3.78	5.08, 7.93
$\Delta\rho$ (e Å^{-3})	1.07, −1.09[d]	0.35, −0.57	1.28, −1.45	0.50, −0.75	0.34, −0.44

[a] Diffractions with $I_o > 2\sigma(I_o)$. [b] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w(F^2) = [\sum\{w(F_o^2 - F_c^2)^2\}/\sum w(F_o^2)^2]^{1/2}$. [c] The solvate was refined without hydrogen atoms (see Experimental Section). [d] Residual electron density in the space accommodating the disordered solvate molecules. [e] Corrected for absorption; transmission coefficient range 0.160−0.619. [f] Flack's enantiomorph parameter: −0.015(4). [g] Corrected for absorption; transmission coefficient range 0.231−0.506.

3 CO]$^+$), 637 ([M − 4 CO]$^+$), 370 (FcPPh$_2$)$^+$. Anal. Calcd for $C_{31}H_{28}FeNO_4PW$: C, 49.70; H, 3.77; N, 1.87. Found: C, 49.69; H, 3.73; N, 1.77.

Analytical data for [1′-(diphenylphosphino-*κP*)ferrocenecarboxaldehyde]pentacarbonyltungsten(0) (**8**) are as follows. ^{1}H NMR (CDCl$_3$): δ 4.38−4.41 (m, 4 H), 4.58 (apparent t, 2 H), 4.64 (apparent dt, 2 H) (4 × C*H*, fc); 7.40−7.48 (m, 10 H, P*Ph*$_2$), 9.43 (s, 1 H, C*H*O). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 70.79, 73.19 (d, J_{PC} = 7 Hz), 74.71, 74.97 (d, J_{PC} = 12 Hz) (4 × *C*H, fc); 79.74 (*C*−CHO, fc); 80.99 (d, $^1J_{PC}$ = 43 Hz, *C*P, fc); 128.37 (d, J_{PC} = 10 Hz), 130.31 (d, J_{PC} = 2 Hz), 132.41 (d, J_{PC} = 12 Hz) (3 × *C*H, PPh$_2$); 137.46 (d, $^1J_{PC}$ = 44 Hz, C_{ipso}, PPh$_2$); 193.21 (*C*═O), 197.12 (d, $^2J_{PC}$ = 7 Hz), 198.45 (d, $^2J_{PC}$ = 22 Hz) (2 × *C*≡O). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 11.1 (s; ^{183}W satellites, $^1J_{WP}$ = 247 Hz). IR (CHCl$_3$): ν/cm^{-1} $\nu_{C\equiv O}$ 2072 s, 1984 m, 1937 br vs; $\nu_{C=O}$ 1684 m, 1665 m. MS (EI): *m/z* 722 (M^+), 694 ([M − CO]$^+$), 666 ([M − 2 CO]$^+$), 638 ([M − 3 CO]$^+$), 610 ([M − 4 CO]$^+$), 582 ([M − 5 CO]$^+$).

Reactions of 2a and 7 with Carbon Monoxide. A solution of carbene in CDCl$_3$ (**2a**, 20 mg/1 mL; **7**, 8.5 mg/1 mL) was stirred under CO (1 atm) at room temperature for 1 day. The solution was filtered trough a 0.45 μm PTFE syringe filter and immediately analyzed by ^{1}H and ^{31}P NMR spectroscopy. In both cases the spectra revealed only unchanged carbenes.

Synthesis of [*N*,*N*-Diethyl-1′-(diphenylphosphino-*κP*)-ferrocenecarboxamide]tetracarbonyliron(0), [Fe(CO)$_4$-{Ph$_2$PfcC(O)NEt$_2$-*κP*}] (9). A solution of sodium naphthalenide prepared as above from sodium (72 mg, 3.1 mmol) and naphthalene (408 mg, 3.2 mmol) in THF (6 mL) was added via a syringe into a solution of iron pentacarbonyl (0.16 mL, 0.8 mmol) in THF (6 mL) at −78 °C. The reaction mixture was warmed to 0 °C, stirred at this temperature for 30 min, cooled to −78 °C, and treated with a solution of **1a** (328 mg, 0.7 mmol) in THF (2 mL). The mixture was warmed to 0 °C, stirred for 30 min at 0 °C, and then cooled to −78 °C. Trimethylchlorosilane (0.3 mL, 2.4 mmol) was added and the solution stirred at −78 °C for another 30 min. The cooling bath was removed, and the mixture was stirred for 1 h without external cooling. Then, neutral alumina (1 g) was added, THF was removed under reduced pressure, and the residue was dried under high vacuum to remove all volatiles. The residue was mixed with light petroleum (2 mL) and the suspension transferred onto a column filled with neutral alumina (15 g). Naphthalene was eluted with hexane. A subsequent elution with dichloromethane gave **9** as an orange solid (250 mg, 56%).

^{1}H NMR (CDCl$_3$): δ 1.10, 1.12 (2 × br s, 3 H, *Me*); 3.30, 3.37 (2 × br s, 2 H, C*H*$_2$); 3.69 (apparent t, 2 H), 4.24 (apparent t, 2 H), 4.61−4.65 (m, 4 H) (4 × C*H*, fc); 7.39−7.59 (m, 10 H, P*Ph*$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 12.81, 14.63 (br, *Me*); 40.71, 42.64 (*C*H$_2$); 71.11, 71.53, 75.04 (d, J_{PC} = 10 Hz), 75.93 (d, J_{PC} = 11 Hz) (4 × *C*H, fc); 77.09 (d, $^1J_{PC}$ ≈ 50 Hz, *C*P, fc; partly obscured by the solvent signal); 81.50 (*C*−CO, fc); 128.16 (d, J_{PC} = 10 Hz), 130.44 (d, J_{PC} = 2 Hz), 132.49 (d, J_{PC} = 10 Hz) (3 × *C*H, PPh$_2$); 137.58 (d, $^1J_{PC}$ = 52 Hz, C_{ipso}, PPh$_2$), 168.43 (*C*═O), 213.20 (d, $^2J_{PC}$ = 19 Hz) (*C*≡O). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 66.9 (s). IR (CHCl$_3$): ν/cm^{-1} $\nu_{C\equiv O}$ 2049 vs, 1975 s, 1941 vs; $\nu_{C=O}$ 1615 m. MS: *m/z* 603 ([M − CO]$^+$), 581 ([M − 2 CO]$^+$), 553 ([M − 3 CO]$^+$), 525 ([M − 4 CO]$^+$), 469 ([Ph$_2$PfcC(O)NEt$_2$]$^+$). HR MS (EI): calcd for $C_{32}H_{28}{}^{52}Cr^{56}FeNO_6P$ ([M − 3 CO]$^+$), 553.0556; found, 553.0550.

X-ray Crystallography. X-ray-quality crystals were obtained by diffusion of pentane into a dichloromethane solution (**2a**·CH_2Cl_2, red prism, 0.28 × 0.28 × 0.35 mm^3) or similarly from pentane/CHCl$_3$ (**2b**, red-orange plate, 0.08 × 0.20 × 0.53 mm^3) and hexane/CHCl$_3$ (**6**·CHCl$_3$, red plate, 0.09 × 0.15 × 0.35 mm^3; **7**, orange prism, 0.15 × 0.35 × 0.40 mm^3; **9**, red plate, 0.08 × 0.10 × 0.30 mm^3). Full-set diffraction data ($\pm h,\pm k,\pm l$) with $2\theta \leq 55.0°$ for all compounds were collected on a Nonius KappaCCD diffractometer equipped with a Cryostream cooler (Oxford Crysoystems) at 150 K using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) and analyzed with the HKL program package.[27]

The structures were solved by direct methods (SIR92[28]) and refined by weighted full-matrix least squares on F^2 (SHELXL97[29]). Final geometric calculations were carried out with a recent version of the Platon program.[30] All non-hydrogen atoms were refined with anisotropic thermal motion parameters. The hydrogen atoms were included in the theoretical positions (C−H bond lengths: 0.93 (aromatic), 0.97 (methylene) and 0.96 (methyl) C) and assigned U_{iso}(H) =

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1.2[U_{eq}(C)] (aromatic and methylene) or 1.5[U_{eq}(C)] (methyl). Solvating dichloromethane in the structure of **2a**·CH_2Cl_2 is extensively disordered and was modeled as if being contributed from two positions (one of which adopted two orientations, ratio 0.80:0.20) to sum up to one solvate molecule per the complex molecule. Due to the complex nature of the disorder, the solvating molecules were included in the model without the hydrogen atoms. Relevant crystallographic data and data on structure refinement are given in Table 5. CCDC reference numbers: CCDC-225468 (**2a**·CH_2Cl_2), CCDC-225469 (**2b**), CCDC-225470 (**7**), CCDC-225471 (**6**·$CHCl_3$), and CCDC-225472 (**9**).

Acknowledgment. This work was financially supported by the Grant Agency of the Czech Republic (Grant Nos. 203/01/P002, 203/99/M037, and 203/04/0487) and is a part of a long-term research plan of the Faculty of Science, Charles University. The Grant Agency of the Czech Republic also sponsored access to the Cambridge Structural Database (Grant No. 203/02/0436).

Supporting Information Available: A drawing of the molecular structure of **7** and full listings of the refined atomic coordinates, anisotropic thermal motion parameters, calculated hydrogen coordinates, bond distances, and bond angles for all crystallographically characterized compounds; these data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

OM040007F