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Tungsten Carbyne Complexes Containing 1,1′-Bis(diphenylphosphino)ferrocene (dppf). Reverse Relationship between NMR Chemical Shifts of the Carbyne ^{13}C and the ^{183}W Nuclei and Molecular Structure of $WCl(CO)_2(dppf)(CPh)$

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The Fischer-type carbyne complexes containing 1,1′-bis(diphenylphosphino)ferrocene (dppf), $WX(CO)_2(dppf)(CR)$ [X = Cl, R = Me, Ph, thienyl, furyl, and ferrocenyl; X = Br; R = ferrocenyl], were synthesized. In these complexes, an increase in the ^{183}W and a decrease in the carbyne ^{13}C chemical shifts with increasing π-donating ability of the carbyne substituents were observed. The ferrocenyl-substituted derivate showed the more enhanced redox potential compared with the corresponding carbonyl analog. The structure of $WCl(CO)_2(dppf)(CPh)$ has been determined by the single-crystal X-ray diffraction method. The crystal is monoclinic with space group $P2_1/n$, and the cell constants are a = 15.565(3) Å, b = 21.493(4) Å, c = 11.167(2) Å, β = 92.45(1)°, and Z = 4. The structure has been refined to a final R value of 0.052. The coordination geometry around the W atom is octahedral with a cis chelation of dppf. The W–C bond distance [1.82(1) Å] is in the normal range. The Cp rings of the dppf ligand in the complex take a staggered conformation, but all the C atoms in each ring are almost coplanar.

Introduction

Complexes which have a multiple bond between the carbon and the transition metal atoms attract much attention in organometallic chemistry. Since the finding of the chromium carbene complex by Fischer,[1] the chemistry of the carbene complexes has been investigated extensively from the various viewpoints.[2,3] On the other hand, the chemistry of the carbyne complexes[4] is not enough exploited yet in spite of the convenient synthetic route by Mayr.[5] The information concerning their physicochemical properties is less available because of the instability of the carbyne complexes, though the electronic state of the metal center and the property of the metal–carbon multiple bond are the factors controlling the reactivity of the carbyne complexes. The NMR data, especially of ^{13}C and metal nuclei, are an important probe for examining the electronic structure around the metal center in the metal complexes. Hafner and the co-workers[6] measured the NMR spectrum of the ^{53}Cr nucleus in carbene complexes, from which the electronic state of the metal center was discussed. The ^{183}W NMR spectrum was reported only about a Schrock-type carbyne complex.[7] We report here the synthesis of a new stable Fischer-type carbyne complex containing 1,1′-bis(diphenylphosphino)ferrocene (dppf) according to the modified method by Mayr and their ^{13}C and ^{183}W NMR spectra.

Results and Discussion

Preparation. Tungsten acyl complex $[NMe_4][(CO)_5WC(O)Me]$ (**1a**)[8] was allowed to react with oxalyl chloride in dichloromethane at −78 °C under N_2, followed by addition of 6 equiv of pyridine to form a cis-substituted bis(pyridine)–carbyne complex,[5] which was treated with dppf in THF at room temperature without isolation to give **2a** as yellow needles in 84% yield. The corresponding phenyl (Ph) (**2b**), thienyl (Th) (**2c**), furyl (Fu) (**2d**), and ferrocenyl (Fc) (**2e**) derivatives were similarly obtained in good yields (Scheme 1). By using oxalyl bromide instead of oxalyl chloride, the bromo analog **3e** was synthesized in good yield by the same procedure. The structures of these carbyne complexes were determined by the NMR

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Table 1. Melting Points, Yields, UV–Vis Spectra and Elemental Analysis for Complexes 2 and 3

compd	mp (°C)	yield (%)	λ_{max} (nm) (ϵ) (in CH_2Cl_2)		found (calcd) (%) C	found (calcd) (%) H
2a	184	84		431.5 (35)	52.99 (53.27)	3.56 (3.65)
2b	208	92	325.0 (1240)	435.0 (50)	56.19 (56.20)	3.71 (3.62)
2c	201	52	343.5 (874)	440 (sh) (40)	54.00 (53.93)	3.53 (3.67)
2d	215 (dec)	39	345.0 (1220)	440 (sh) (80)	53.37 (54.18)	3.36 (3.43)
2e	208	63	316.0 (1440)	466.5 (138)	53.98 (54.15)	3.63 (3.61)
3e	200	70	318.5 (814)	470 (237)	52.77 (52.70)	3.75 (3.48)

Table 2. ^1H NMR Spectral Data for Complexes 2 and 3 (400 MHz, $CDCl_3$)

complex	dppf H_α	dppf H_β	phenyl	substituents
2a	4.27 (s, 2H) 4.30 (s, 2H)	4.38 (s, 2H) 4.70 (s, 2H)	7.25–7.90 (m, 20H)	1.61 (t, J_{PH} = 4.4 Hz, 3H, Me)
2b	4.29 (s, 2H) 4.33 (s, 2H)	4.45 (s, 2H) 4.75 (s, 2H)	7.24–7.90 (m, 20H)	6.60 (d, J = 7.5 Hz, 2H, *o*-Ph) 7.03 (t, J = 7.5 Hz, 2H, *m*-Ph) 7.17 (t, J = 7.5 Hz, 1H, *p*-Ph)
2c	4.28 (s, 2H) 4.32 (s, 2H)	4.44 (s, 2H) 4.71 (s, 2H)	7.23–7.85 (m, 20H)	6.42 (d, J = 4.2 Hz, 1H, Th H_5) 6.69 (t, J = 4.2 Hz, 1H, Th H_3) 7.05 (d, J = 4.2 Hz, 1H, Th H_4)
2d	4.28 (s, 2H) 4.31 (s, 2H)	4.50 (s, 2H) 4.69 (s, 2H)	7.25–7.90 (m, 20H)	5.71 (d, J = 3.3 Hz, 1H, Fu H_5) 6.11 (dd, J = 3.3, 1.8 Hz, Fu H_3) 7.14 (d, J = 1.8 Hz, 1H, Fu H_4)
2e	4.27 (s, 2H) 4.29 (s, 2H)	4.37 (s, 2H) 4.64 (s, 2H)	7.25–7.90 (m, 20H)	3.83 (t, J = 1,7 Hz, 2H, Fc H_α) 4.00 (t, J = 1.7 Hz, 2H, Fc H_β) 4.23 (s, 5H, Fc $H_{1'}$)
3e[a]	4.27 (s, 2H) 4.33 (s, 2H)	4.34 (s, 2H) 4.70 (s, 2H)	7.30–7.90 (m, 20H)	3.99 (t, J = 1.7 Hz, 2H, Fc H_α) 4.08 (t, J = 1.7 Hz, 2H, Fc H_β) 4.26 (s, 5H, Fc $H_{1'}$)

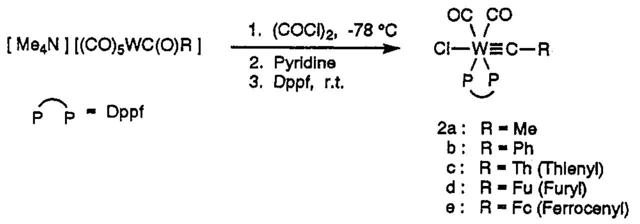
[a] in CD_2Cl_2

Table 3. ^{13}C NMR Spectral Data for Complexes 2 and 3 (100 MHz, $CDCl_3$)

complex	dppf	W–CO	W–C	substituent
2a	72.09 (t, J = 3.3 Hz), 72.52 (t, J = 3.3 Hz) 75.17 (t, J = 5.0 Hz), 75.64 (t, J = 5.0 Hz) 76.20 (d+t, J = 44.9, 33.2 Hz)	210.53 (d+t, J = 41.3, 19.3 Hz)	274.74 (t, J = 9.9 Hz)	35.5 (s, CH_3)
2b	72.20 (t, J = 2.4 Hz), 72.63 (t, J = 2.4 Hz) 75.43 (t, J = 4.7 Hz), 75.66 (t, J = 4.7 Hz) 76.13 (d+t, J = 44.1, 34.1 Hz)	210.57 (d+t, J = 42.1, 18.9 Hz)	267.20 (t, J = 9.6 Hz)	127.48 (s, *m,p*-Ph) 129.80 (s, *o*-Ph) 148.92 (s, ipso Ph)
2c	72.17 (s), 72.60 (s) 75.56 (t, J = 5.4 Hz), 75.66 (t, J = 5.4 Hz) 76.10 (d+t, J = 44, 34 Hz)	210.46 (d+t, J = 43.2, 19.1 Hz)	251.05 (t, J = 11.6 Hz)	125.96, 126.11 133.16, 153.36
2d	72.22 (t, J = 3.6 Hz), 72.59 (t, J = 3.6 Hz) 75.52 (t, J = 4.9 Hz), 75.70 (t, J = 4.9 Hz) 76.10 (d+t, J = 44, 34 Hz)	210.30 (d+t, J = 43.1, 19.3 Hz)	247.57 (t, J = 11.2 Hz)	127.97, 133.14 141.38, 163.52
2e	72.10 (s), 72.50 (s) 75.43 (t, J = 5.1 Hz), 75.64 (t, J = 5.1 Hz) 76.60 (d+t, J = 43.2, 33.1 Hz)	212.18 (d+t, J = 43.2, 21.6 Hz)	269.23 (s)	66.13 (s, Fc H_α) 69.24 (s, Fc $H_{1'}$) 70.18 (s, Fc H_β)
3e[a]	72.67 (s), 73.10 (s) 76.06 (t, J = 5.1 Hz) 76.86 (d+t, J = 43.2, 40.7 Hz)	211.36 (m)		69.02 (s, Fc H_α) 69.77 (s, Fc $H_{1'}$) 70.75 (s, Fc H_β)

[a] In CD_2Cl_2

Scheme 1



spectra and elemental analyses. The yields, melting points, electronic spectra, and elemental analysis data are summarized in Table 1. The ^1H and ^{13}C NMR data are summarized in Tables 2 and 3, respectively. The ^1H NMR spectrum of **2e**, for example, showed the Cp ring protons of the ferrocenyl group at δ 3.83 (t, 2H, J = 2 Hz), 4.00 (t, 2H, J = 2 Hz) and 4.27 (s, 5H), the Cp ring protons of dppf at 4.27 (s, 2H), 4.29 (s, 2H), 4.37 (s, 2H), and 4.64 (s, 2H), and phenyl protons at 7.36 (m, 12H) and 7.80 (m, 8H).

The ^{13}C NMR spectrum of **2e** exhibited the signals of the carbyne and the carbonyl carbons at δ 269.23 and 212.18, respectively. Complexes **2a**, **2b**, and **2e** were stable in dichloromethane, while **2c** and **2d** were unstable, especially **2d** which decomposed after a prolonged time even in dichloromethane saturated with Ar.

Cyclic Voltammogram. The ferrocenyl derivative **3e** showed two reversible redox waves at $E_{1/2}$ = +0.47 [**3e**$^+$/**3e**$^{2+}$] and +0.07 V [**3e**/**3e**$^+$] vs {FcH/FcH$^+$} in 0.1 M $[(C_4H_9)_4N]ClO_4/CH_2Cl_2$ at room temperature, which were assigned to the $Fe^{II/III}$ redox reaction in the dppf and ferrocenyl moieties, respectively. The corresponding potentials in the similar chloro complex **2e** were $E_{1/2}$ = +0.51 and +0.105 V. The large electronegativity of the chloro ligand compared with the bromo ligand seemed to be responsible for the high-potential shift observed in **2e**. The redox potential of the ferrocenyl group in complex **3e** was less positive than that of the tetracarbonyl analog

Table 4. Selected NMR Data for WCl(dppf)(CO)$_2$(CR) (2)

complex	^{13}C NMR (δ, ppm)^a W–CR	^{13}C NMR (δ, ppm)^a W–CO	^{31}P NMR^b (δ, ppm) [J_{pw} (Hz)]	^{183}W NMR^c (δ, ppm) [J_{pw} (Hz)]
2a	274.74	210.53	16.27 (240)	−1583 (244)
2b	267.20	210.57	16.28 (240)	−1443 (240)
2c	251.05	210.46	16.27 (240)	−1373 (243)
2d	247.57	210.29	16.52 (241)	−1365 (243)
2e	269.23	212.18	16.28 (238)	*d*

[a] Solvent: CDCl$_3$. Coupling constants were omitted. [b] An external reference: 85% H$_3$PO$_4$. Solvent: CDCl$_3$. [c] An external reference: Na$_2$WO$_4$ (1 M) in D$_2$O at pD ~10. Solvent: CD$_2$Cl$_2$–CD$_2$Cl$_2$. [d] No data were available because of the low solubility.

WBr(CO)$_4$(CFc) (4) with an $E_{1/2}$ [4/4$^+$] of +0.28 V.[9] This seemed to be due to the more enhanced π-back-donation from the W atom to the carbyne carbon in the dppf complex than in the (CO)$_2$ complex. If the correlation of $E_{1/4}$ to σ_p proposed by Hoh et al.[10] stands for these carbyne complexes, a value of σ_p = +0.16 can be obtained for the –CWBr(CO)$_2$(dppf) group, which is fairly smaller than that for the –CWBr(CO)$_4$ moiety of 4 (σ_p = +0.65).[9] The σ_p values obtained indicated that the former group had a smaller electron-withdrawing effect on the ferrocenyl moiety compared with that of the latter.

Electronic Spectra. The UV–vis spectral data of the carbyne complexes **2a**–**2e** in CH$_2$Cl$_2$ are summarized in Table 1. Complexes **2a**–**2e** showed two absorption bands near 440 (ϵ 35–237) and 325–345 nm (ϵ 814–1440). According to the band assignment of the alkylidyne complexes X(CO)$_2$L$_2$W≡CR by Bocarsly et al.[11] the more intense band near 330 nm and the longer-wavelength band near 440 nm were assigned to π–π^* transitions of the metal—carbon triple bond and the d–π^* transitions around the metal center, respectively. However, the latter band may be overlapped with the d–d transition of ferrocene,[12] since it was also observed in other dppf-containing derivatives. The band near 440 nm in the ferrocenyl derivate **2e** showed some red shift (ca. 25 nm), suggesting an interaction between the occupied d orbital of the iron atom of the ferrocenyl group and the empty p orbital of the carbyne carbon (corresponding to the α-position of the ferrocene derivatives). The red shift of the d–π^* and π–π^* transitions after replacement of an alkyl group by a phenyl group in X(CO)$_2$L$_2$W≡CR was observed and was considered to reflect the considerable conjugation of the M≡C π-system with the phenyl ring.[13] The absorptions near 330 nm in **2a**–**2e** were clearly dependent on the substituent on the carbyne carbon atom and shifted to the longer-wavelength side in the following sequence: Me < Fc < Ph < Th < Fu, the order of which is consistent with that of the π-electron-donating ability. The order is also in agreement with that of the high-field shift of the carbyne carbon in the ^{13}C NMR spectra (vide infra).

NMR Spectra. The ^{31}P, ^{183}W, and selected ^{13}C NMR data of complexes **2a**–**2e** are summarized in Table 4. As shown in Table 4, the chemical shift of the carbonyl carbon atom remains nearly unchanged in all complexes. Also in the ^{31}P NMR spectra all the complexes exhibited similar chemical shifts near δ 16 and coupling constants $J(^{31}\mathrm{P}–^{183}\mathrm{W})$ = 240 Hz for the phosphine signals of dppf. This indicates that the effect of the substituent on the carbyne carbon does not reach beyond the W atom. On the other hand, the carbyne carbon signal was observed in the range from δ 250 to 280 with increasing chemical shift in the sequence **2a** < **2e** < **2b** < **2c** < **2d**. A linear relationship was observed between the chemical shift of the carbyne carbon and that of the cyano carbon in the corresponding nitriles R–CN, except for the methyl derivative (correlation coefficient = 0.992). The result suggests that the π-electron-donating ability of the substituent on the carbyne or cyano carbon may be responsible for such a shift of the carbon signals, since the methyl group is not a π but a σ electron donor.

^{183}W signals (16.67 MHz, CD$_2$Cl$_2$–CH$_2$Cl$_2$) of carbyne complexes **2a**–**2d** were observed at δ −1365 to −1583 (reference: Na$_2$WO$_4$ in D$_2$O) as triplets with the coupling constants $J(^{183}\mathrm{W}–^{31}\mathrm{P})$ = 240–244 Hz, which were consistent with those observed in the ^{31}P NMR spectra (Table 4). The signal was not available for complex **2e** because of the low solubility in CH$_2$Cl$_2$. Those chemical shifts showed the following characteristic features: a deshielding effect of the carbyne ligand, an influence of the substituent on the carbyne, and a good correlation with the ^{13}C chemical shifts of the carbyne carbon.

For the W(0) complexes, the ^{183}W chemical shift of dppf complex (dppf)W(CO)$_4$ was δ −3023, which was similar to those of other bis(phosphine) complexes of tungsten (δ −3055 to −2978),[14] while W(CO)$_6$ gave a signal at δ −3486. This suggests that the replacement of two CO groups by a dppf causes a deshielding effect by about 400 ppm and the dppf ligand containing a Fe atom likely gives no specific electronic influence compared with other bis(phosphine) ligands. The formal oxidation number of the W atom in the present Fischer type of carbyne complexes is +4 according to the definition of Collmann et al., where the carbyne ligand has a formal charge of −3.[15] The consideration was supported by the X-ray crystallographic data on the W≡C bond in a carbyne complex, the bond length of which is almost coincident to the sum of halves of the W≡W and C≡C lengths.[3b] The ^{183}W chemical shift of CpWH$_2$ (δ −4663) is only one example for mononuclear complexes with the formal oxidation state of +4.[16] In the present carbyne complexes tungsten nuclei are far deshielded compared with this instance. Young and co-workers observed ^{183}W signals for the Schrock-type carbyne complex with the formal oxidation state of +6 at δ +2526 to +3613,[7] and these were positioned almost at the lower shielding edge in chemical shifts of tungsten(VI) complexes ranging from δ −1117 to +3769.[17,18] Those observations indicated that the carbyne ligand, regardless of the type of carbyne complex, causes a fairly large low-field shift of the ^{183}W signals.

Although both of the ^{183}W and ^{13}C chemical shifts depend strongly on the substituent on the carbyne carbon, ^{183}W signals appeared in the lower field accordingly as carbyne carbon signals went to higher shielding, and they correlated linearly with each other except for the meth-

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ylcarbyne complex **2a** (correlation coefficient = 0.997). The shielding constant σ controlling the chemical shift of the metal nucleus is given by the following Ramsey equation.[19,20]

$$\sigma = \sigma^{d} + \sigma^{p}$$

In the diamagnetic early transition metal complexes, the σ^{p} (temperature-independent paramagnetic) term is claimed to have a larger contribution than the σ^{d} (diamagnetic) term.[20b,21] The σ^{p} term reflects the extent of participation of the electron on the p and d orbitals and is represented by the following equation.[19]

$$\sigma^{p} = -B\langle r^{-3}\rangle/\Delta\epsilon$$

where $\Delta\epsilon$ is the HOMO–LUMO gap affected by the ligand strength, $\langle r^{-3}\rangle$ is related to the nephelauxetic effect, and B corresponds to the imbalance of electron density at the nucleus, e.g. covalency of the metal–ligand bond and the π-bond formation. Therefore, if the ^{183}W chemical shift in the present complexes was mainly due to σ^{p}, the observed shift could be a measure of the decrease of the π-back-donation on the metal nucleus. Since $\Delta E = h\nu$, σ^{p} ought to be proportional to the wavelength of the UV–vis absorption band of the metal–carbyne bond. In fact, the peak wavelength of the pπ–pπ^* absorption band observed near 330 nm in the carbyne complexes **2b**–**2e** (vida supra) shifted with the ^{183}W chemical shift. This seems to support the main contribution of the σ^{p} term to the ^{183}W resonance of the carbyne complexes.

The metal–carbyne bond consists of one σ-donation from a carbyne carbon and two π-back-donations to a carbyne carbon. The magnitude of the π-electron-donating ability of the substituent on the carbyne carbon may be reflected in the amount of π-electron flowing into the empty p orbital on the carbyne carbon, which may compete with the π-back-donation from the W metal. The π-back-donation, therefore, decreases according to the following order of increasing π-electron-donating ability: Fc < Ph < Th < Fu (vide supra). The decrease of W–C bond order brings about the upfield shift of the ^{13}C signals and the downfield shift of the ^{183}W signals. This is also consistent with the observation that the ^{183}W signals in the W(0) low-valent complexes shift to a deshielding side as the π-back-donation becomes smaller,[22] which is predominantly controlled with the temperature-independent paramagnetic shielding.

X-ray Analysis. The structure of complex **2b** was determined by X-ray analysis. The ORTEP drawing of **2b** is shown in Figure 1. The crystallographic data and the selective bond distances and angles are listed in Tables 5 and 6, respectively. The W atom is coordinated in a somewhat distorted octahedral configuration with the Cl atoms trans to the carbyne ligand. The dppf ligand is in a cis configuration as in the bis(pyridine) complex, WBr(CO)$_2$(Py)$_2$(CPh) (**5**).[23] The W–CO bond distances, 2.00(1) and 2.01(1) Å, in **2b** are the same as those in complex **5**. The W–P bond distances of 2.583(2) and 2.585(2) Å in **2b** are somewhat longer than those (average 2.467(2) Å) in the tetrakis(phosphine) complex, WCl(PMe$_3$)$_4$(CH),[24] probably due to the difference in electron-donating ability of the trans ligands. The W–C bond distance is 1.82(1) Å, closely similar to that (1.84 Å) in the bis(pyridine) complex **5**, but fairly different from that in the tetracarbonyl complex, WI(CO)$_4$(CPh) [1.90(5)[25] and 1.88(10) Å[26]]. The C(carbyne)–C(Ph) distance adjacent to the W–C bond of 1.45(1) Å is shorter than that in the bis(pyridine) complex **5** (1.50(2) Å), probably reflecting the avoidance of the steric repulsion between the phenyl groups caused by the steric crowding of the dppf ligand. The bond angles

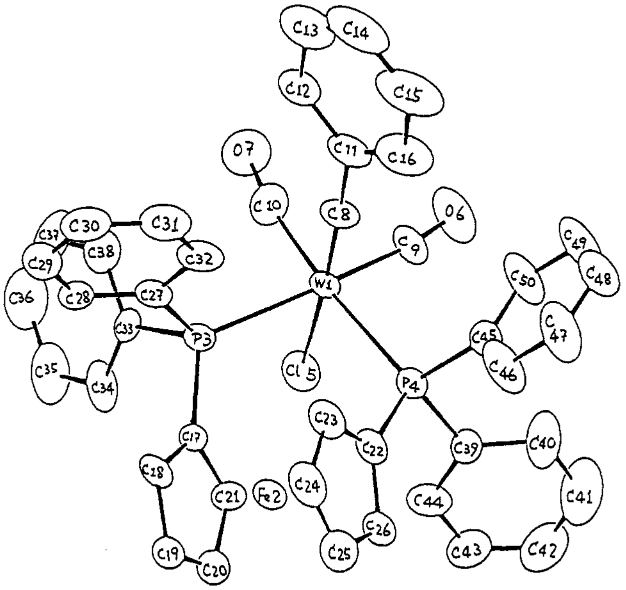

Figure 1. View of complex **2b** with selected numbering.

Table 5. Crystallographic Data for 2b

chemical formula	$C_{41}H_{31}ClO_2P_2FeW$
fw	924.90
cryst size (mm^3)	0.20 × 0.10 × 0.10
unit-cell dimens	
a (Å)	15.565(3)
b (Å)	21.493(4)
c (Å)	11.167(2)
β (deg)	92.45(1)
vol of unit cell (Å^3)	3732(1)
cryst syst	monoclinic
space group	$P2_1/n$ (No. 14)
Z value	4
densities (g/cm^3): D_{obs}; D_{calc}	1.60; 1.65
$F(000)$	1760
linear abs coeff (cm^{-1})	34.87 (Mo Kα)
diffractometer used	Mac Science MXC18
radiation [λ (Å)]	Mo Kα (0.710 69)
max (sin θ)/λ	0.651
total no. of reflns measd	9503
no. of unique reflns	8640
internal consistency: R_{int}	0.08
function minimized	$\Sigma[w(F_o^2 - F_c^2)^2]$, $w = 1.0/[(\sigma F_o)^2 + 0.0001F_o^2$
no. of reflns used ($F > 5.00(F)$))	4959
no. of variables	461
residuals: R; R_w	0.052; 0.046
goodness of fit: S	1.44
max shift/esd in final cycle	0.12
max negative peak in final diff map (e/Å^3)	−1.26
max positive peak in final diff map (e/Å^3)	2.04

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Table 6. Selected Bond Distances (Å) and Angles (deg) for Complex 2b (Esds in Parentheses)

	Distances		
W(1)–P(3)	2.583(2)	P(4)–C(22)	1.80(1)
W(1)–P(4)	2.585(2)	P(4)–C(39)	1.83(1)
W(1)–Cl(5)	2.508(2)	P(4)–C(45)	1.83(1)
W(1)–C(8)	1.82(1)	C(8)–C(11)	1.45(1)
W(1)–C(9)	2.00(1)	C(9)–O(6)	1.14(1)
W(1)–C(10)	2.01(1)	C(10)–O(7)	1.15(1)
P(3)–C(17)	1.816(9)	Cp1···Fe(2)	1.637
P(3)–C(27)	1.83(1)	Cp2···Fe(2)	1.639
P(3)–C(33)	1.821(9)		
	Angles		
C(8)–W(1)–C(9)	90.8(4)	P(3)–W(1)–C(9)	166.4(3)
C(8)–W(1)–C(9)	86.5(4)	P(3)–W(1)–C(10)	88.8(3)
C(8)–W(1)–Cl(5)	173.9(3)	P(3)–W(1)–Cl(5)	82.45(8)
C(8)–W(1)–P(3)	99.0(3)	P(3)–W(1)–P(4)	97.85(8)
C(8)–W(1)–P(4)	93.8(3)	P(4)–W(1)–C(9)	90.8(3)
W(1)–C(8)–C(11)	173.7(8)	P(4)–W(1)–C(10)	173.2(3)
W(1)–P(3)–C(17)	118.7(3)	P(4)–W(1)–Cl(5)	91.84(8)
W(1)–P(4)–C(22)	118.0(3)		

around the W atom are almost normal for the octahedral geometry. The W–C(8)–C(11) is nearly linear (173.7(8)°). These bond parameters of **2b** are not likely to suggest a certain contribution of the vinylidene type of resonance form which plays an important role in the amino–carbyne complex, $[Cr(CO)_5(CNMe_2)]BF_4$.[27] Contrary to such X-ray structural parameters, the ^{183}W NMR chemical shift seems to provide a sensitive probe for the electronic state of the carbyne complexes.

In complex **2b**, the two Cp rings of the dppf ligand hold a staggered conformation in which the torsion angle P(3)–Cp(1)–Cp(2)–P(4) is 33.4° but are nearly coplanar (tilting angle, 1.9°). Upon complexation with transition metals, the dppf ligand generally suffers a conformational change (to an eclipsed conformation),[28–34] while free dppf takes a staggered conformation with a trans arrangement of PPh_2 groups.[35] The final conformation of Cp rings in dppf seems to depend on the compatibility of the bite angle of dppf and the size of the metal ion, because the strain in the dppf complexes is relieved by the twisting and/or tilting of the Cp rings with each other. In complex **2b**, the Cp rings are staggered with a twist angle of 2.75° from an exactly staggered conformation. Other complexes having the staggered conformation of the Cp rings were reported in 1-[(dppf)Pd]B_3H_7[36] and (dppf)$Mo(CO)_4$,[37] in which the twist angles are 9 and 5.9°, respectively. The P(3)–W–P(4) bond angle is 97.25°, which is slightly larger than that observed in (dppf)$Mo(CO)_4$ [P–Mo–P angle, 95.28(2)°] and slightly smaller than that in 1-[(dppf)Pd]-B_3H_7 [P–Pd–P angle, 104.2(7)°]. This trend cannot be always explained only by the bite angle P–M–P, because the average W–P distance of 2.584(2) Å in **2b** is longer than the average Mo–P distance of 2.560(16) Å in (dppf)-$Mo(CO)_4$. Finally, the W–Fe distance of 4.8 Å is too long to interact with ech other directly.

Experimental Section

The melting points were measured by differential scanning calorimetry (Seiko DSC-20). The electronic spectra were measured by using a Shimadzu UV 2000. The cyclic voltammetry was carried out using a Huso 311B potentiostat and 321B potential sweep unit with a glassy carbon working, an Ag/Ag^+ (NO_3^-, 0.01 M in CH_3CN) reference, and a Pt counter electrodes in CH_2Cl_2 containing $(n\text{-}Bu)_4NClO_4$ (0.1 M) as supporting electrolyte. Potentials noted in this text are of those calculated vs ferrocene/ferrocenium (FcH/FcH^+). The NMR spectra were recorded on a Bruker AM 400. The ^{1}H and ^{31}P NMR spectra were measured in $CDCl_3$ by using TMS as the internal standard and 95% H_3PO_4 as the external standard, respectively. The ^{183}W spectra (16.44 MHz) were measured in CD_2Cl_2–CH_2Cl_2 by using Na_2WO_4 in D_2O (pD ~ 11) as the external standard.

The ammonium salts of the tungsten acyl complexes $[(CO)_5Cr{=}C(R)ONMe_4]$ (R = Me,[7] Ph,[7] Fu,[38] Th,[38] and Fc[39]) were prepared according to Fisher's method.

Chlorodicarbonyl[1,1′-bis(diphenylphosphino)ferrocene-*P,P*]phenylcarbynyltungsten(II). General Procedure. To a solution of $[(CH_3)_4N][W(CO)_5COPh]$ (0.5 g, 1 mmol) in dry dichloromethane (20 mL) was added oxalyl chloride (0.1 mL, 1.3 mmol) by using injector under N bubbling at −78 °C. After stirring for 30 min, the temperaure was raised to 0 °C. Pyridine (0.65 mL, 8 mmol) was added, and the solution was stirred for 2 h at room temperature. After evaporation, the residue was dissolved in dry THF (30 mL). After dppf (0.56 g, 1 mmol) had been added, the solution was stirred for 1.5 h at 50 °C. After evaporation, the residue was chromatographed on alumina by elution of hexane–dichloromethane to give **2a** as orange crystals, which was recrystallized from dichloromethane–hexane (0.9 g, 98%).

Tetracarbonyl[1,1′-bis(diphenylphosphino(ferrocene-*P,P*]tungsten(0). A solution of $W(CO)_6$ (1.0 g, 2.8 mmol) and dppf (1.6 g, 2.8 mmol) in dry dichloromethane–acetone (2:1, 300 mL) was irradiated by a high-pressure Hg lamp (450 W) for 2 h. After evaporation, the residue was chromatographed on alumina by elution of hexane–dichloromethane to give the title complex, which was recrystallized from benzene (1.2 g, 42%).

Structure Determination. Crystal data for **2b**: $C_{41}H_{31}ClO_2P_2FeW$, M = 924.90, monoclinic, space group $P2_1/n$, a = 15.565(3) Å, b = 21.493(4) Å, c = 11.167(2) Å, β = 92.45(1)°, V = 3732(1) Å^3, Z = 4, D_x = 1.65 g cm^{-3}, linear absorption coefficient 34.87 cm^{-1}, $F(000)$ = 1760, crystal size 0.20 × 0.10 × 0.10 mm.

Data collection was performed at room temperature on a Mac Science MXC18 diffractometer using graphite-monochromated Mo $K\alpha$ (λ = 0.710 69 Å) radiation by the ω-scan method. A total of 9503 reflections were collected, and 4956 independent reflections with $F > 5.00\sigma(F)$ were used for structure solution by Patterson and difference Fourier methods and subsequent refinement. Hydrogen atoms were included in structure factor calculations (standard geometry, 0.98 Å). Refinement with anisotropic temperature factors for non-hydrogen atoms using a total of 461 variables converged at R = 0.052, R_w = 0.046.

Supplementary Material Available: Tables of crystal data, positional and thermal parameters, bond distances and angles, and least-squares planes and deviations therefrom and diagrams showing the unit cell packing in **2b** (30 pages). Ordering information is given on any current masthead page.

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