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Articles

Reduction of a Coordinated Acetonitrile Ligand: Synthesis of an Ethylimido Complex of Tungsten

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Treatment of the dinitrogen complex $W(N_2)_2(dppe)_2$ (**1**; dppe = 1,2-bis(diphenylphosphino)ethane) with trifluoromethanesulfonic acid yields the novel hydrazido complex $[W(N_2H_2)(OTf)(dppe)_2]^+[OTf]^-$ (**2**; OTf = $CF_3SO_3^-$). The triflato ligand is readily displaced by other ligands and coordinating solvents. The triflato complex **2** yields the complex $[W(N_2H_2)(NCCH_3)(dppe)_2]^{2+}$ (**5**), when it is dissolved in acetonitrile, and **5** is readily deprotonated by a variety of bases to give the acetonitrile−dinitrogen complex $W(N_2)(NCCH_3)(dppe)_2$ (**3**). Complex **3** is protonated at the β-carbon by tetrafluoroboric acid, resulting in the reduction of the coordinated nitrile to give the novel imido complex $[WF(NCH_2CH_3)(dppe)_2]^+[BF_4]^-$ (**4**). The X-ray crystal structure of the imido complex **4** reveals an effectively linear W−N−C bond (171.8°) in the imido ligand with a W−N bond length of 1.741(4) Å.

Introduction

There has been considerable interest in the reduction of small, unsaturated nitrogen-containing molecules at molybdenum and tungsten dinitrogen binding centers.[1] A range of hydrazido,[2] aminocarbyne,[3] and carbyne/alkylidene[4] complexes have been prepared via the reduction of coordinated dinitrogen, isonitrile, and alkynyl ligands, respectively, under protic conditions. In some systems, the N≡N or C≡N bond of the coordinated dinitrogen or isonitrile ligand undergoes complete reductive cleavage to yield free amines or alkanes.[5] Although the products from the reductive cleavage of nitriles have also been detected,[6] no analogous imido complexes derived from the β-protonation of coordinated organonitriles have yet been reported.

There has also been considerable work employing transition-metal imido complexes[7] as an important class of compounds for stoichiometric and catalytic transformations. (Organoimido)tungsten complexes have been prepared via a number of methods, including reactions of metal complexes with isocyanates,[8] deprotonation of amine/amido ligands,[9] and nucleophilic attack at the β-carbon of nitrile ligands.[10]

In this paper we describe the synthesis of the complex $W(N_2)(NCCH_3)(dppe)_2$ (**3**; dppe = 1,2-bis(diphenylphosphino)ethane), from $W(N_2)_2(dppe)_2$ (**1**), by an indirect route via the hydrazido complex $[W(N_2H_2)(OTf)(dppe)_2]^+$ (**2**; OTf = $CF_3SO_3^-$). Protonation of the acetonitrile ligand affords a novel imido complex, $[WF(NCH_2CH_3)(dppe)_2]^+$ (**4**), effectively reducing the coordinated nitrile (Scheme 1).

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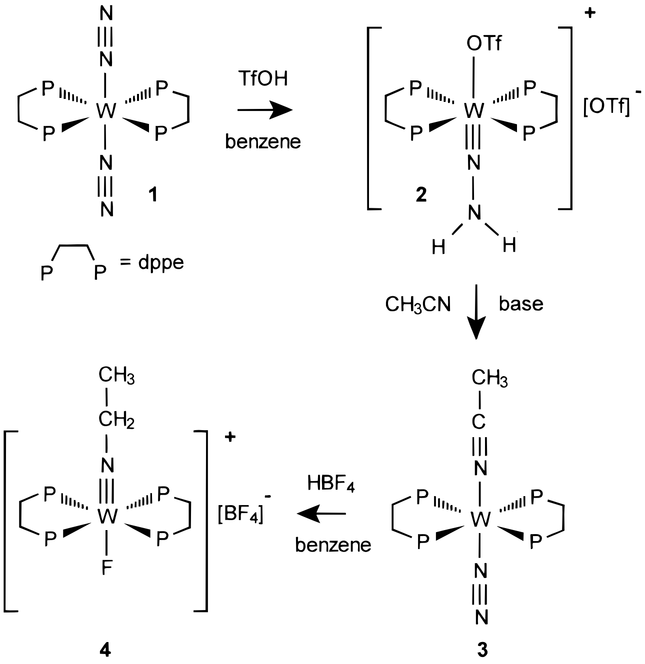
Scheme 1



Results and Discussion

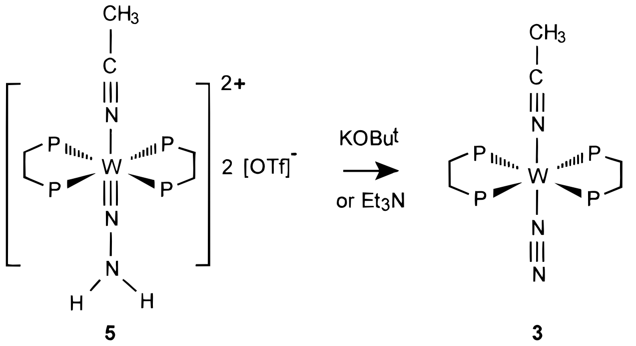
A number of hydrazido complexes of the type [W$(N_2H_2)X(dppe)_2]^+Y^-$ (X = Y = Cl, Br, tosylate; X = F, Y = $BF_4)^{2a,c,5i,11}$ have been prepared from the reaction of the bis(dinitrogen) complex $W(N_2)_2(dppe)_2$ (**1**), with the acid HY. The novel hydrazido complex $[W(N_2H_2)(OTf)(dppe)_2]^+[OTf]^-$ (**2**; $OTf^- = CF_3SO_3^-$) was similarly prepared from the reaction of **1** with trifluoromethanesulfonic acid in benzene (Scheme 1). The reaction proceeded in moderate yield (64%) at room temperature to give **2** as a light brown crystalline solid.

The complex **2** exhibited a single peak in the $^{31}P\{^1H\}$ NMR spectrum at δ 37.9 ppm with tungsten satellites ($^1J_{W-P}$ = 284.5 Hz), indicating that the phosphorus atoms were chemically equivalent and occupied the four equatorial coordination sites. Apart from the resonances of the dppe ligand, the $^1H\{^{31}P\}$ NMR spectrum exhibited a broadened singlet at δ 5.11 ppm, which was assigned to the protons on the hydrazido ligand. The protons of the hydrazido ligand underwent rapid H/D exchange in methanol-d_4.

The presence of two distinct triflate environments, one coordinated triflato ligand and one triflate counterion, was confirmed by ^{19}F NMR spectroscopy. The ^{19}F NMR spectrum consisted of two singlet resonances of equal intensity, with the coordinated triflate (δ −73.1 ppm) appearing to slightly lower field than the counterion (δ −75.2 ppm). The coordinated triflato ligand was readily displaced in coordinating solvents such as acetonitrile and methanol.

When the hydrazido complex **2** was dissolved in acetonitrile, the triflato ligand was displaced to yield the intermediate complex $[W(N_2H_2)(NCCH_3)(dppe)_2]^{2+}$ (**5**). On treatment with base, (KO^{t}Bu, Et_3N, or $NaBH_4$/EtOH), **5** was deprotonated to yield the dinitrogen-acetonitrile complex $W(N_2)(NCCH_3)(dppe)_2$ (**3**)[12] in good yield (76%) (Scheme 2).

Scheme 2



Reaction of the dinitrogen complex **3** with tetrafluoroboric acid in benzene at room temperature resulted in protonation at the β-carbon of the acetonitrile ligand to yield the ethylimido complex $[WF(NCH_2CH_3)(dppe)_2]^+[BF_4]^-$ (**4**), as an orange crystalline solid. The reduction of the nitrile moiety was accompanied by a formal four-electron oxidation of the W(0) center, resulting in the formation of a W≡N triple bond.

The ethylimido complex **4** was fully characterized by multinuclear NMR and X-ray crystallographic studies. The $^{31}P\{^1H\}$ NMR spectrum of **4** exhibited a fluorine-coupled doublet at δ 33.6 ppm ($^2J_{P-F}$ = 44.5 Hz) and tungsten satellites ($^1J_{P-W}$ = 293.0 Hz). The single resonance confirms that the phosphorus atoms occupy the four equivalent equatorial coordination sites around the tungsten atom. The ^{19}F NMR spectrum exhibited two signals. The low-field signal (δ −149.9 ppm) appeared as a broad singlet and was assigned to the tetrafluoroborate counterion. The high-field signal (δ −174.8 ppm) appeared as a quintet with $^2J_{P-F}$ = 44.5 Hz and was assigned to the metal-bound fluoro ligand.

In addition to the resonances of the dppe ligand, the $^1H\{^{31}P\}$ NMR spectrum exhibited a triplet at δ −0.30 ppm with $^3J_{H-H}$ = 7.4 Hz and a doublet of quartets at δ 1.91 ppm with $^3J_{H-H}$ = 7.4 Hz and $^4J_{H-F}$ = 3.7 Hz. The high-field resonance collapsed to a singlet upon selective decoupling of the resonance at δ 2.25 ppm and was assigned to the CH_3−group of the ethylimido ligand. The resonance at δ 2.25 ppm was assigned to the $-CH_2-$ group of the imido ligand. ^{13}C NMR confirmed the presence of a CH_3CH_2- moiety, exhibiting a resonance for the CH_3 group at δ 14.1 ppm and for the CH_2 group at δ 57.8 ppm.

X-ray crystallographic studies confirmed the structure of complex **4**. The complex adopts a slightly distorted octahedral geometry about the tungsten center with the tungsten displaced from the least-squares equatorial plane by 0.18 Å toward the imido axial ligand (Figure 1).

Selected bond distances and angles are shown in Table 1. The four phosphorus atoms occupy the equatorial coordination sites of the tungsten center and have very similar bond lengths. The ethylimido and fluoro ligands occupy the remaining axial coordination sites, in a trans configuration.

The W(1)−N(1)−C(1) bond angle of 171.8° is essentially linear and is typical of complexes containing

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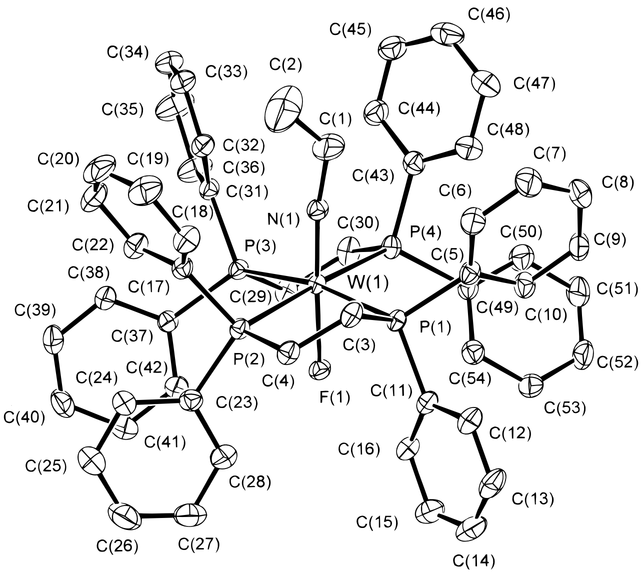

Figure 1. ORTEP diagram of $[WF(NCH_2CH_3)(dppe)_2]^+$-$[BF_4]^-$ (**4**), showing atom labeling (25% ellipsoids).

Table 1. Selected Bond Distances (Å) and Angles (deg) for $[WF(NCH_2CH_3)(dppe)_2]^+[BF_4]^-$ (4)

W(1)−N(1)	1.741(4)	W(1)−F(1)	2.008(2)
W(1)−P(1)	2.511(1)	W(1)−P(2)	2.519(1)
W(1)−P(3)	2.517(1)	W(1)−P(4)	2.511(1)
N(1)−C(1)	1.456(7)	C(1)−C(2)	1.28(1)
W(1)−N(1)−C(1)	171.8(4)	N(1)−W(1)−F(1)	177.7(1)
N(1)−W(1)−P(1)	87.2(1)	N(1)−W(1)−P(2)	91.5(1)
N(1)−W(1)−P(3)	104.0(1)	N(1)−W(1)−P(4)	92.9(1)
P(1)−W(1)−F(1)	91.35(8)	P(1)−W(1)−P(2)	79.66(4)
P(1)−W(1)−P(3)	168.77(4)	P(1)−W(1)−P(4)	101.67(4)
P(2)−W(1)−F(1)	90.10(8)	P(2)−W(1)−P(3)	99.74(4)
P(2)−W(1)−P(4)	175.48(4)	P(3)−W(1)−F(1)	77.43(8)
P(3)−W(1)−P(4)	78.10(4)	P(4)−W(1)−F(1)	85.56(8)

Table 2. W−N Bond Lengths (Å) and W−N−R Bond Angles (deg) of Selected Tungsten Complexes (R = C, N)

complex	W−N	W−N−R
$[W(N_2H_2)Cl(dppe)_2]^+[BPh_4]^-$ [a]	1.73(1)	171(1)
$[W(N_2HCH_3)Br(dppe)_2]^+Br^-$ [b]	1.768(14)	174(1)
$W(NPh)Cl_2(PMe_3)_3$[c]	1.755(3)	179.5(3)
$W(NC_6H_3Pr^i{}_2{-}2,6)Cl_3(dppe)$[d]	1.758(7)	172.9(1)
$W(NCH_2CH{=}CH_2)Cl_2(PPh_2Me)_2(CO)$[e]	1.746(5)	170.1(6)
$W\{NC(Br)C(CN)C(CN)_2\}Br(dppe)_2$[f]	1.777(6)	171.4(5)
$[W(NCH_2CH_3)F(dppe)_2]^+[BF_4]^-$	1.741(4)	171.8(4)

[a] Reference 13. [b] Reference 14. [c] Reference 8a. [d] Reference 8b. [e] Reference 8c. [f] Reference 10a.

imido or hydrazido ligands[7] (Table 2). The slight deviation from linearity may reflect contact with the C17−C22 and C31−C36 phenyl residues. The distance from C2 to C32 is 3.55 Å, and that from C2 to C18 is 3.76 Å. The W(1)−N(1) bond length of 1.741 Å is also typical of a metal-nitrogen triple bond[7] (Table 2). It is noteworthy that the W−N bond length and the W−N−C bond angle are very similar to the corresponding values for the analogous hydrazido complex $[W(N_2H_2)Cl(dppe)_2]^+[BPh_4]^-$ [13] which was prepared from the bis(dintirogen) complex **1** by the protic reduction of a coordinated dinitrogen ligand. C(2) has a notably large thermal ellipsoid in the structure, and this could be the result of disorder or high thermal motion and could contribute to the apparently short C(1)−C(2) bond.

Although imido complexes of tungsten and molybdenum have been synthesized by other methods,[8−10] the isolation and characterization of the ethylimido complex **4** represents the first example of the preparation of an imido complex from the protic reduction of a nitrile ligand. The analogous β-protonation of isoelectronic ligands (dinitrogen,[2] isonitriles,[3] and acetylides[4]) at metal centers has been well-established, and the preparation of complex **4** effectively completes this series.

The stepwise approach to the acetonitrile−dinitrogen species **3** via the hydrazido complex **2** provides a thermal route from the bis(dinitrogen) complex **1**. The protonation of one dinitrogen ligand permits substitution of the other. This approach is potentially applicable to the synthesis of a wide variety of substituted hydrazido or dinitrogen complexes.

Summary

The hydrazido complex $[W(N_2H_2)(OTf)(dppe)_2]^+[OTf]^-$ was synthesized by the protonation of the dinitrogen complex $W(N_2)_2(dppe)_2$ with trifluoromethanesulfonic acid. Displacement of the triflato ligand and deprotonation of the hydrazido moiety afforded the acetonitrile complex $W(NCCH_3)(N_2)(dppe)_2$. Protonation of $W(NCCH_3)(N_2)(dppe)_2$ with ethereal tetrafluoroboric acid proceeded at the nitrile carbon, resulting in the reduction of the acetonitrile to an ethylimido ligand to give the complex $[WF(NCH_2CH_3)(dppe)_2]^+[BF_4]^-$ (**4**). The reduction was accompanied by a formal four-electron oxidation of the tungsten center, resulting in the formation of the tungsten−nitrogen triple bond.

Experimental Section

General Procedures. All manipulations were performed under an inert atmosphere of nitrogen, either by use of standard Schlenk and vacuum line techniques or by performing reactions in a nitrogen-filled drybox. All solvents were degassed and distilled under a nitrogen atmosphere from a suitable drying agent. $W(N_2)_2(dppe)_2$ was synthesized by following the method of Hussain et al.[15] NMR spectra were recorded using a Bruker AMX400 spectrometer and were recorded at 300 K. ^1H NMR (400.13 MHz) and ^{13}C NMR (100.61 MHz) chemical shifts were referenced to internal solvent residuals. ^{31}P NMR (161.98 MHz) NMR chemical shifts were referenced to external, neat trimethyl phosphite, taken as δ 140.85 ppm. ^{19}F NMR (376.43 MHz) chemical shifts were referenced to external, neat hexafluorobenzene, taken as δ −163.0 ppm. Elemental analyses were performed at the Australian National University Research School of Chemistry (Canberra, Australia) and Campbell Microanalytical Laboratories, University of Otago (Dunedin, New Zealand).

Synthesis of *trans*-Bis[1,2-bis(diphenylphosphino)ethane]hydrazido(triflato)tungsten Triflate, $[W(OTf)(N_2H_2)(dppe)]^+[OTf]^-$ (2). Trifluoromethanesulfonic acid (220 mg, 1.45 mmol) was added to a solution of $W(N_2)_2(dppe)_2$ (**1**; 0.60 g, 580 μmol) in benzene (40 mL). The reaction mixture was stirred at room temperature for 3 h, and the solvent was removed in vacuo to give a brown oily residue. The residue was dissolved in tetrahydrofuran (5 mL), and the addition of

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(14) March, F. C.; Mason, R.; Thomas, K. M. *J. Organmet. Chem.* **1975**, *96*, C43.

(15) Hussain, W.; Leigh, G. J.; Ali, H. M.; Pickett, C. J.; Rankin, D. A. *J. Chem. Soc., Dalton Trans.* **1984**, 1703.

ether (15 mL) resulted in the precipitation of a light brown solid, which was isolated by filtration and recrystallized from tetrahydrofuran-ether. $[W(OTf)(N_2H_2)(dppe)_2]^+[OTf]^-$ (**2**) was obtained as a light brown crystalline solid (490 mg, 64%), mp 275−277 °C.

Anal. Found: C, 49.6; H, 3.9; N, 2.3. Calcd for $C_{54}H_{48}F_6N_2O_6P_4S_2W$: C, 49.6; H, 3.7; N, 2.1. ^1H NMR (thf-d_8): δ 3.04 (m, 8H, PC**H**$_2$), 5.11 (s(br), 2H, N**H**$_2$), 7.03, 7.23−7.45 (m, 40H, P(C$_6$**H**$_5$)$_2$) ppm. $^{31}P\{^1H\}$ NMR (thf-d_8): δ 37.9 (s (W satellites, d, $^1J_{W-P}$ = 284.5 Hz)) ppm. $^{13}C\{^1H,^{31}P\}$ NMR (thf-d_8): δ 31.8 (s, P**C**H$_2$), 130.8, 131.4, 132.7, 132.9, 134.4, 135.3, 136.0, 136.2 (8 × s, P(**C**$_6$H$_5$)$_2$) ppm. ^{19}F NMR (thf-d_8): δ −73.1 (s, 3F, W−**OTf**), −75.2 (s, 3F, $^-$OTf) ppm.

Reaction of 2 with acetonitrile-d_3: Synthesis of *trans-(*Acetonitrile)hydrazidobis[1,2-bis(diphenylphosphino)ethane]tungsten $[W(NCCD_3)(N_2H_2)(dppe)]^{2+}$ (5). $[W(N_2H_2)(OTf)(dppe)_2]^+[OTf]^-$ (**2**; 20 mg, 15 μmol) was dissolved in acetonitrile-d_3 (500 μL, 432 μmol) to yield a purple solution of $[W(NCCD_3)(N_2H_2)(dppe)]^{2+}$ (**5**), which was characterized by NMR spectroscopy.

^1H NMR (CD_3CN): δ 2.56 (m, 4H, PC**H**$_2$C**H**$_2$P), 2.95 (m, 4H, PC**H**$_2$C**H**$_2$P), 5.97 (s(br), 2H, N$_2$**H**$_2$), 6.70−7.47 (m, 40H, P(C$_6$**H**$_5$)$_2$) ppm. $^{31}P\{^1H\}$ NMR (CD_3CN): δ 39.2 (s (W satellites, d, $^1J_{W-P}$ = 278.8 Hz)) ppm. $^{13}C\{^1H,^{31}P\}$ NMR (CD_3CN): δ 29.9 (s, P**C**H$_2$), 128.2, 129.3, 129.5, 130.6, 131.3, 131.7, 132.1, 132.7 (8 × s, P(**C**$_6$H$_5$)$_2$)) ppm. ^{19}F NMR (CD_3CN): δ −74.8 (s, $^-$**OTf**) ppm.

Synthesis of *trans*-(Acetonitrile)(dinitrogen)bis[1,2-bis(diphenylphosphino) ethane]tungsten, $W(NCCH_3)(N_2)(dppe)_2$ (3). $[W(N_2H_2)(OTf)(dppe)_2]^+[OTf]^-$ (**2**; 300 mg, 230 μmol) was dissolved in acetonitrile (10 mL) and stirred for 15 min. A solution of sodium borohydride (26 mg, 690 μmol) in ethanol (1 mL) (or Et_3N (2.1 equiv) or KO^{t}Bu (2.1 equiv)) was added, and the reaction mixture was stirred at room temperature for 30 min. The resulting dark red precipitate was isolated by filtration, washed with acetonitrile (2 mL) and ethanol (2 mL), and dried in vacuo. $W(N_2)(NCCH_3)(dppe)_2$ (**3**) was obtained as a red crystalline solid (182 mg, 76%), mp 192−194 °C (dec).

IR (Nujol): 2174 (w(br), C≡N), 1886 (w(br), N$_2$) cm^{-1}. ^1H NMR (C_6D_6): δ 1.48 (s, 3H, C**H**$_3$CN), 2.27 (m, 4H), 2.44 (m, 4H, PC**H**$_2$C**H**$_2$P), 6.86−7.44 (m, 40H, P(C$_6$**H**$_5$)$_2$) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 48.94 (s (W satellites, d, $^1J_{W-P}$ = 328 Hz)) ppm. $^{13}C\{^1H,^{31}P\}$ NMR (C_6D_6): δ 5.0 (s, **C**H$_3$CN), 32.6 (s, P**C**H$_2$**C**H$_2$P), 112.1 (s, CH$_3$**C**N), 128.7−142.0 (8 × s, P(**C**$_6$H$_5$)$_2$) ppm.

Reaction of 3 with tetrafluoroboric acid in benzene: Synthesis of *trans*-(Ethylimido)fluorobis[1,2-bis(diphenylphosphino)ethane]tungsten tetrafluoroborate, $[WF(NCH_2CH_3)(dppe)_2]^+[BF_4]^-$ (4). Tetrafluoroboric acid (32 μL, 230 μmol, 7.13 M in diethyl ether) was added to a solution of $W(N_2)(NCCH_3)(dppe)_2$ (**3**; 95 mg, 91 μmol) in benzene (30 mL) at room temperature. The reaction mixture was stirred for 1 h and filtered through a sintered-glass frit. Addition of ether (20 mL) to the filtrate precipitated a yellow solid, which was isolated by filtration. The residue was washed with hexane (3 mL), thf (1 mL), and hexane (3 mL) and dried in vacuo. Recrystallization from ethanol afforded $[WF(NCH_2CH_3)(dppe)_2]^+[BF_4]^-$ (**4**) as an orange crystalline solid (60 mg, 58%), mp 275 °C (dec).

Anal. Found: C, 57.3; H, 4.6; N, 1.1. Calcd $C_{54}H_{53}BF_5NP_4W$: C, 57.4; H, 4.7; N, 1.2. ^1H NMR ($CDCl_3$): δ −0.30 (t, 3H, $^3J_{H-H}$ = 7.4 Hz, C**H**$_3$CH$_2$N), 1.91 (dq, 2H, CH$_3$C**H**$_2$N, $^3J_{H-H}$ = 7.4 Hz, $^4J_{H-F}$ = 3.7 Hz), 2.62 (m, 4H, PC**H**$_2$C**H**$_2$P), 2.78 (m, 4H, PC**H**$_2$C**H**$_2$P), 7.10−7.39 (m, 40H, P(C$_6$**H**$_6$)$_2$) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 33.6 (d, $^2J_{F-P}$ = 44.5 Hz (W satellites, dd, $^1J_{W-P}$ = 293.0 Hz, $^2J_{F-P}$ = 44.5 Hz)) ppm. $^{13}C\{^1H,^{31}P\}$ NMR ($CDCl_3$): δ 14.1 (s, **C**H$_3$CH$_2$N), 32.5 (s, P**C**H$_2$**C**H$_2$P), 57.8 (s, CH$_3$**C**H$_2$N), 129.7, 130.2, 131.8, 132.1, 134.0, 134.3, 135.1, 135.7 (8 × s, P(**C**$_6$H$_5$)$_2$) ppm. ^{19}F NMR ($CDCl_3$): δ −174.8 (qu, 1F, $^2J_{F-P}$ = 44.6 Hz, W**F**), −149.9 (br s, 4F, B**F**$_4$$^-$) ppm.

Table 3. Crystallographic Data for $[WF(NCH_2CH_3)(dppe)_2]^+[BF_4]^-$ (4)

empirical formula	$C_{54}H_{53}BF_5NP_4W$
fw	1129.57
cryst color, habit	orange, prism
cryst dimens	0.35 × 0.09 × 0.08 mm
lattice param	a = 12.237(2) Å b = 13.946(3) Å c = 16.422(2) Å α = 88.82(1)° β = 77.09(1)° γ = 66.48(2)° V = 2497.4(9) Å^3
space group	$P\bar{1}$ (No. 2)
Z	2
D_{calcd}	1.502 g/cm^3
F_{000}	1136.00
μ(Mo Kα)	25.00 cm^{-1}
radiation	Mo Kα (λ = 0.71069 Å), graphite monochromated
temperature	21.0 °C
$2\theta_{max}$	49.9°
hkl range	−14 to 14, −16 to 16, 0−19
no. of rflns measd	9125
no. of unique rflns	8787 (R_{int} = 0.018)
no. of observns ($I > 3.00\sigma(I)$)	7300
no. of variables	595
residuals: R; R_w^{a}	0.031; 0.032
goodness-of-fit indicator	1.49
max peak in final diff map	1.09 e/Å^3
min peak in final diff map	−0.74 e/Å^3

^{a} $R = \sum(|F_o| - |F_c|)^2/\sum|F_o|$. $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$. $w = 1/\sigma^2(F_o)$.

X-ray Crystallography. Crystals of $[WF(NCH_2CH_3)(dppe)_2]^+[BF_4]^-$ (**4**) suitable for X-ray crystallography were obtained by careful recrystallization from ethanol. An orange prismatic crystal having approximate dimensions 0.35 × 0.09 × 0.08 mm was attached to a thin glass fiber and mounted on an Enraf-Nonius CAD4 diffractometer employing graphite-monochromated Mo Kα radiation (Table 3). Primitive triclinic cell constants were obtained from a least-squares refinement using the setting angles of 25 reflections in the range $18.98 < 2\theta < 23.88°$. Diffraction data were collected at a temperature of 21 ± 1 °C using ω−$^4/_3\theta$ scans to a maximum 2θ value of 49.9°. The intensities of three representative reflections, measured every 60 min, did not change significantly during the data collection. An analytical absorption correction was applied, and the data were also corrected for Lorentz and polarization effects.

All calculations were undertaken with the teXsan[16] crystallographic software package. Neutral atom scattering factors were taken from Cromer and Waber.[17] Anomalous dispersion effects were included in F_c,[18] and the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[19] The values for the mass attenuation coefficients were those of Creagh and Hubbell.[20] The structure was solved by heavy-atom Patterson methods[21]

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(16) teXsan: Crystal Structure Analysis Package; Molecular Structure Corp., The Woodlands, TX, 1985 & 1992.

(17) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A.

(18) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.

(19) Creagh, D. C.; McAuley, W. J. In *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Vol C, Kluwer Academic: Boston, 1992; Vol. C. Table 4.2.6.8, pp 219−222.

(20) Creagh, D. C.; Hubbell, J. H. In *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic: Boston, 1992; Vol. C, Table 4.2.4.3, pp 200−206.

and expanded using Fourier techniques.[22] Non-hydrogen atoms were modeled with anisotropic thermal parameters. Hydrogen atoms were included in the model at calculated positions with group thermal parameters. Slight residual electron density in the vicinity of the BF_4^- counterion suggests minor orientational disorder, which was not modeled. An ORTEP projection of the molecule is provided in Figure 1.[23]

Supporting Information Available: Tables S1−S8, giving all bond distances and angles, atomic coordinates, and thermal parameters for complex **4** (15 pages). Ordering information is given on any current masthead page.

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(22) DIRDIF94: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. The DIRDIF-94 Program System, Technical Report of the Crystallography Laboratory; University of Nijmegen, Nijmegen, The Netherlands, 1994.

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