MSm/e[relativeintensity]480[M⁺,1.3],440[(M-C₄H₄)⁺, 100], 124 [CpCo⁺, 40.9], 77 [Ph⁺, 24.6], 65 [Cp⁺, 8.8], 59 [Co⁺, 16.4]; Anal. found (calcd. for $C_{33}H_{25}Co$): C, 82.5 (82.5); H, 5.7 (5.3).

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11. Cyclic voltammograms were measured at room temperature in CH_2Cl_2 with (n-Butyl)₄N⁺PF₆⁻ as a conducting salt. Working electrode, platimum disc; auxiliary electrode, platinum wire; reference electrode, Ag/AgCl.

Molecular Structure of W(N'Bu)(CO)(PPh₂Me)₂Cl₂

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Since the first nitrene complexes, OsO_3 (NR), were reported in 1959, transition-metal nitrene (or imido) complexes have received continuous interest.[1] For instance, high valent imido complexes can activate C-H bonds of several compounds.[2] Recently, Mayer's group reported that heterocumulenes such as isocyanates and carbodiimides react with $WCl_2(PPh_2Me)_4$ under mild conditions to form imido-carbonyl and imido-isonitrile complexes, respectively (Eq. 1).[3] These reactions were remarkable in that a formal double bond is cleaved to form a divalent and a neutral ligand. Very recently, Bergman and his workers reported an insertion of CO into an Ir≡N bond in Cp*Ir(≡N'Bu)(Cp*=C₅(CH₃)₅), which is the first carbonylation of a terminal imido ligand to give an isocyanate complex.[4] The results of above studies prompted us to investigate the possibility of insertion reactions of CO into other terminal metal nitrene centers. We set out insertion reactions of carbon monoxide into W≡NR bonds. We report here the molecular structure of *trans*, *cis*-W(PPh₂Me)₂Cl₂(N'Bu)(CO).

$$(1)$$
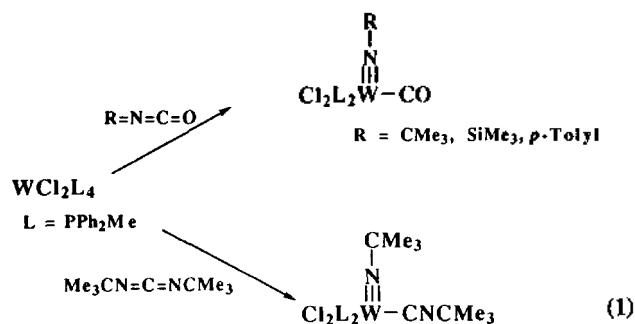
Experimental

Unless otherwise stated, all the reactions have been performed with standard Schlenk line and cannula techniques

Table 1. Crystallographic data and summary of data collection and structure refinement

formula	$C_{31}H_{35}NOP_2Cl_2W$	F (000)	1496
fw	754.29	no. of	2511
crystal system	monoclinic	unique data	
space group	$P2_1$	no. of reflns	2503
a, Å	10.731 (2)	used, I>2 σ (I)	
b, Å	21.371 (5)	no. of params	258
c, Å	13.851 (3)	Z	4
β, deg	90.40 (2)	scan range	3<2θ<50°
V, Å³	3716 (1)	scan type	ω-2θ
d_{calc}, g cm⁻³	1.577	GOF on F²	1.048
μ, mm⁻¹	3.930	R	0.0428
Max. in Δρ (e A³⁻)0.60		wR₂ᵃ	0.0956

$$^a wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_c^2)^2]\}^{1/2}$$

under an argon atmosphere. Carbonylation reactions have been performed in a 60 mL of quartz pressure vessel (Kontes). CO (99.9%) was purchased from Union Gas Co. and used as received. Trimethylphosphine (PMe₃; Me=CH₃, 1 M in toluene) and trimethylphosphite (P(OMe)₃) were purchased from Aldrich Co. and used as received. The title complex, **I**, was prepared by the literature method.[2]

X-ray Structure. All X-ray data were collected with use of an Enraf-Noinus CAD4 automated diffractometer equipped with a Mo X-ray tube and a graphite crystal monochromator. Details on crystal and intensity data are given in Table 1. The orientation matrix and unit cell parameters were determined from 25 machine-centered reflections with 16<2θ< 27°. Axial photographs were used to verify the unit cell choice. Intensities of three check reflections were monitored after every 1 h during data collection. Data were corrected for Lorentz and polarization effects. The intensity data were empirically corrected with Ψ-scan data. All calculations were carried out on the personal computer with use of the SHE-LXS-86,[5] SHELXL-93[6] programs.

A brown crystal, shaped as a plate, of approximate dimensions 0.15×0.38×0.42 mm, was used for crystal and intensity data collection. The unit cell parameters and systematic absences, 0k0 (k=2n+1), indicated two possible space groups: of $P2_1$ and $P2_1/m$.. A statistical analysis of intensities of reflections suggested a noncentrosymmetric space group and the structure converged only in the space group $P2_1$. The structure was solved by the heavy atom methods. The W, Cl, and P atoms were refined anisotropically. The phenyl groups were treated as isotropic rigid groups. All hydrogen atoms were positioned geometrically and refined using a riding model. Final atomic positional parameters for non-hydrogen atoms are shown in Table 2 and the selected bond distances and bond angles are shown in Table 3; anisotropic thermal parameters, hydrogen atom coordinates, full bond distances and bond angles, and tables of observed and calculated structure factors are available as supplementary materials.

Results and Discussions

There are two crystallographically independent molecules

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$)

	x	y	z	U (eq)[a]
W(1)	−744 (1)	0	−9937 (1)	36 (1)
Cl(1)	−2130 (7)	−41 (5)	−11376 (5)	71 (3)
Cl(2)	822 (8)	−665 (4)	−10762 (6)	52 (3)
P(1)	184 (7)	926 (4)	−10836 (5)	41 (2)
P(2)	−1917 (8)	−989 (4)	−9550 (5)	37 (2)
O(1)	−3023(30)	807(12)	−9296(21)	98 (8)
N(1)	−144(22)	164(10)	−8780(13)	40 (5)
C(1)	145(35)	322(15)	−7776(23)	62 (8)
C(2)	−714(37)	123(19)	−7156(25)	84 (9)
C(3)	1443(30)	−47(15)	−7494(23)	74 (8)
C(4)	236(33)	1050(13)	−7778(22)	66 (7)
C(5)	346(32)	806(13)	−12137(21)	63 (7)
C(6)	−1794(33)	−1584(14)	−10501(21)	66 (8)
C(7)	−2175(30)	484(14)	−9522(21)	55 (7)
C(11)	−751(15)	1629 (7)	−10729(12)	46 (5)
C(12)	−574(17)	2031 (8)	−9951(12)	54 (6)
C(13)	−1433(21)	2503 (9)	−9772(13)	93(10)
C(14)	−2468(19)	2573 (9)	−10371(15)	85 (9)
C(15)	−2645(16)	2171 (9)	−11149(14)	76 (8)
C(16)	−1786(17)	1699 (8)	−11327(12)	54 (6)
C(21)	1782(13)	1164 (8)	−10544(14)	49 (6)
C(22)	2621(16)	730 (6)	−10169(14)	48 (6)
C(23)	3876(15)	882 (7)	−10085(14)	64 (7)
C(24)	4293(14)	1468 (8)	−10377(14)	57 (6)
C(25)	3454(18)	1901 (6)	−10753(15)	78 (9)
C(26)	2199(17)	1749 (7)	−10836(15)	73 (8)
C(31)	−1329(17)	−1421 (7)	−8515(11)	44 (6)
C(32)	−47(16)	−1494 (8)	−8416(11)	54 (6)
C(33)	436(14)	−1868 (8)	−7683(13)	62 (7)
C(34)	−363(18)	−2169 (7)	−7048(11)	66 (7)
C(35)	−1645(17)	−2096 (8)	−7147(11)	76 (8)
C(36)	−2128(14)	−1722 (9)	−7881(12)	61 (7)
C(41)	−3584(13)	−910 (9)	−9400(12)	53 (7)
C(42)	−4443(15)	−1097 (8)	−10098(10)	48 (6)
C(43)	−5709(14)	−1001 (8)	−9952(10)	60 (6)
C(44)	−6116(13)	−717 (9)	−9108(12)	64 (7)
C(45)	−5257(17)	−530 (9)	−8410(10)	90 (9)
C(46)	−3991(16)	−626 (8)	−8556(11)	63 (7)
W(2)	−4080 (1)	−7706 (1)	−5241 (1)	38 (1)
Cl(21)	−2588 (7)	−7744 (5)	−3865 (5)	70 (3)
Cl(22)	−5536(10)	−7083 (4)	−4283 (7)	63 (3)
P(21)	−5049 (8)	−8648 (4)	−4456 (6)	49 (3)
P(22)	−2944 (8)	−6675 (4)	−5536 (5)	47 (3)
O(2)	−1887(30)	−8523(12)	−6077(20)	95 (7)
N(2)	−4745(25)	−7778(12)	−6387(15)	52 (5)
C(51)	−5093(31)	−7969(14)	−7341(21)	50 (7)
C(52)	−4134(45)	−7683(24)	−7965(30)	112(12)
C(53)	−6323(35)	−7774(18)	−7616(26)	88 (9)
C(54)	−5256(50)	−8608(20)	−7442(34)	118(14)
C(55)	−5014(31)	−8656(13)	−3131(19)	59 (7)
C(56)	−2941(33)	−6177(14)	−4449(21)	65 (7)
C(57)	−2710(33)	−8230(14)	−5730(25)	57 (7)
C(61)	−6708(12)	−8819 (8)	−4691(13)	52 (6)
C(62)	−7230(15)	−9382 (6)	−4395(12)	56 (6)
C(63)	−8508(16)	−9476 (6)	−4477(12)	53 (6)
C(64)	−9265(12)	−9006 (7)	−4853(12)	62 (7)
C(65)	−8743(15)	−8443 (6)	−5149(12)	51 (6)
C(66)	−7465(16)	−8349 (6)	−5067(13)	54 (7)
C(71)	−4242(20)	−9378 (9)	−4753(17)	57 (6)
C(72)	−3097(21)	−9492(10)	−4311(17)	82 (8)
C(73)	−2388(19)	−10005(11)	−4588(18)	128(13)
C(74)	−2824(24)	−10404(11)	−5307(21)	104(11)
C(75)	−3969(26)	−10290(11)	−5749(20)	131(14)
C(76)	−4677(20)	−9777(10)	−5472(18)	87 (9)
C(81)	−3624(15)	−6161 (6)	−6437(10)	38 (5)
C(82)	−4915(15)	−6113 (7)	−6451(10)	54 (7)
C(83)	−5500(12)	−5712 (7)	−7102(11)	49 (6)
C(84)	−4793(15)	−5359 (6)	−7739(10)	53 (6)
C(85)	−3501(15)	−5408 (7)	−7726(10)	58 (6)
C(86)	−2916(12)	−5809 (7)	−7075(11)	53 (6)
C(91)	−1318(15)	−6774 (9)	−5900(13)	33 (5)
C(92)	−369(19)	−6594 (9)	−5271(12)	85 (9)
C(93)	868(17)	−6655(11)	−5545(16)	93(10)
C(94)	1157(16)	−6896(12)	−6449(18)	120(13)
C(95)	208(22)	−7077(11)	−7078(13)	122(13)
C(96)	−1029(19)	−7016 (9)	−6804(12)	81 (8)

[a] U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.
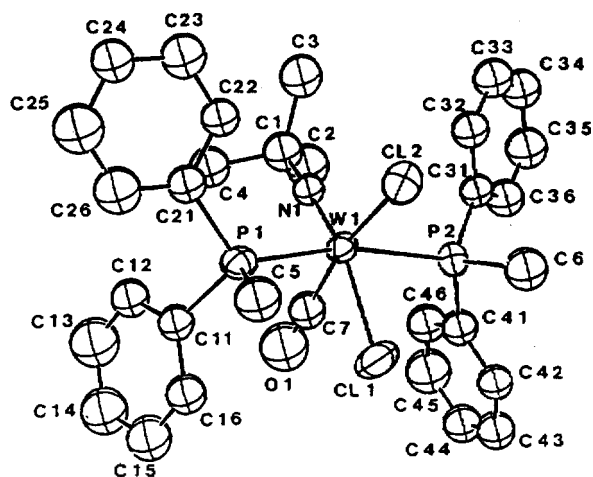
Figure 1. ORTEP drawing of I showing the atom-labeling scheme and 50% probability thermal ellipsoids

in an asymmetric unit with $Z=4$. The molecular structure with the atomic numbering scheme of one of the two identical molecules in the asymmetric unit is shown in Figure 1. The coordination sphere of I can be described as a slightly distorted octahedron, in which an imido, CO, and the two Cl ligands lie on the basal plane and two phosphine groups occupy the axial sites (Table 3). The basal plane adopts an essentially planar geometry with the displacement of an atom being less than 0.016 Å, from the least-squares plane defined by W1, Cl1, Cl2, C7, and N1 atoms. The geometry of I, an octahedral structure with the π-donor and π-acceptor ligands *cis*, was originally assigned on the basis of spectroscopic data

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Notes

Table 3. Selected Bond Distances [Å] and Bond angles [deg]

Bond Distances			
W(1)-N(1)	1.76 (2)	W(2)-N(2)	1.74 (2)
W(1)-Cl(1)	2.480 (5)	W(2)-Cl(21)	2.481 (5)
W(1)-Cl(2)	2.484 (9)	W(2)-Cl(22)	2.449(12)
W(1)-P(1)	2.544 (9)	W(2)-P(22)	2.552 (8)
W(1)-P(2)	2.519 (8)	W(2)-P(21)	2.517 (9)
W(1)-C(7)	1.94 (4)	W(2)-C(57)	1.97 (4)
O(1)-C(7)	1.19 (4)	O(2)-C(57)	1.19 (5)
Bond Angles			
N(1)-W(1)-C(7)	84.8(10)	N(2)-W(2)-C(57)	86.5(12)
N(1)-W(1)-P(1)	98.6 (8)	N(2)-W(2)-P(21)	98.9 (9)
N(1)-W(1)-P(2)	98.8 (8)	N(2)-W(2)-P(22)	97.1 (9)
N(1)-W(1)-Cl(1)	162.4 (8)	N(2)-W(2)-Cl(21)	162.7(10)
N(1)-W(1)-Cl(2)	106.7 (8)	N(2)-W(2)-Cl(22)	106.4 (9)
Cl(1)-W(1)-P(1)	82.5 (3)	Cl(21)-W(2)-P(21)	84.7 (3)
Cl(1)-W(1)-P(2)	81.0 (3)	Cl(21)-W(2)-P(22)	81.1 (3)
C(7)-W(1)-Cl(1)	77.6 (7)	C(57)-W(2)-Cl(21)	76.5 (7)
P(2)-W(1)-P(1)	162.6 (2)	P(21)-W(2)-P(22)	163.5 (2)
Cl(1)-W(1)-Cl(2)	90.8 (3)	Cl(22)-W(2)-Cl(21)	90.7 (3)
Cl(2)-W(1)-P(1)	87.2 (3)	Cl(22)-W(2)-P(21)	86.2 (4)
Cl(2)-W(1)-P(2)	87.6 (3)	Cl(22)-W(2)-P(22)	85.7 (3)
C(7)-W(1)-Cl(2)	168.4 (6)	C(57)-W(2)-Cl(22)	167.0 (7)
C(7)-W(1)-P(1)	92.5(10)	C(57)-W(2)-P(21)	90.3(10)
C(7)-W(1)-P(2)	89.2(10)	C(57)-W(2)-P(22)	94.4(10)
O(1)-C(7)-W(1)	176 (3)	O(2)-C(57)-W(2)	176 (3)
C(1)-N(1)-W(1)	171 (2)	C(51)-N(2)-W(2)	166 (2)

such as ^{31}P-, ^{13}C-, and ^{1}H NMR and IR spectra.[3]

Compound I has two *trans* PPh₂Me groups and two *cis* Cl atoms. Of particular interest are the bonds of the W-NR fragment. The W-N bond distances (1.76 (2), 1.74 (2) Å) of compound I are almost equal to that (1.754 (6) Å of an aryl imido analog, W(N-*p*-C₆H₄CH₃)Cl₂(CO)(PMePh₂)₂.[3b] The W-N-C (*tert*-butyl) bond angles of (171 (2), 166 (2)°) also agree with that (171.6 (5)°) in W(N-*p*-C₆H₄CH₃)Cl₂(CO)(PMePh₂)₂.[3b] The other structurally related complex, W(NPh)Cl₂(CO)(PMe₃)₂, shows the similar bonding parameters of the W-N bond distance and W-N-C bond angle (1.755 (3) Å, 179.5 (3)°).[7] It is a little interesting that bonding parameters of the tungsten-imido fragment do not appear to be sensitive to the nature of the substituents on the imido nitrogen atom. In other words, the W≡NR fragment maintains its geometrical features, regardless of the substituents (an alkyl or aryl group).

It was suggested that, for imido ligands, the metal nitrogen bond order can be inferred from the position of the substituent. A linear M-N-R unit implies that the nitrogen is *sp* hybridized and that there is a metal-nitrogen triple bond, while substantial bending of the M-N-R linkage indicates the presence of a lone pair on the nitrogen and is usually taken as evidence for a reduced bond order.[1a] On the basis of this valence bond description, the nitrogen is *sp* hybridized and the W-N bond has a triple bond character in compound I.

Since the imido and carbonyl groups in I are oriented *cis* to each other, carbonylation reactions *via* a CO insertion into the W-NR bond to transform a terminal imido ligand to an isocyanate ligand were tried (Eq. 2). We hoped that coordination of small ligands with the high coordinating ability such as CO, PMe₃, and P(OMe)₃, might be able to induce the CO insertion in an intramolecular fashion. At room temperature, however, compound I does not react with CO up to 2 atm, and with excess (more than 5-fold excess) PMe₃ and P(OMe)₃, either. The above results indicate that the W-N triple bond is very strong and unreactive.
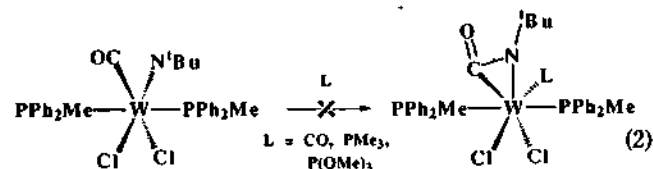
$$(2)$$

Supplementary Materials Available. Tables of bond distances and bond angles, anisotropic thermal parameters, positional parameters for hydrogen atom (7 pages); listings of observed and calculated structure factors (6 pages). Supplementary materials are available from one of the authors (S. W. L.) upon request.

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