in xylene new signals in the ^{31}P NMR spectrum in the same range of chemical shifts (ca. δ +38) that compounds **1**–**3** do. All the efforts to isolate these intermediate species in analytically pure states have been unsuccessful to date. The ^{31}P NMR data do not give any conclusive structural information about them. Moreover, the presence of the four fluorine atoms in the phosphine also complicates the aromatic region in the ^{13}C NMR spectra.

Further investigation on these intermediates is required. It might be more informative to use the homologous compounds with $P(o\text{-}BrC_6H_4)Ph_2$, assuming that they will show similar behavior as the PCBr complexes.

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Registry No. **1**, 96411-10-8; **2**, 112173-10-1; **3**, 112173-11-2; **4**, 112173-12-3; **5**, 112195-84-3; **6**, 96411-08-4; **7**, 112173-13-4; **8**, 112173-14-5; **9**, 112173-15-6; PZ, 288-13-1; 3-MPZ, 1453-58-3; 4-MPZ, 7554-65-6; PCBr, 27384-33-4; Rh(acac)(CO)(PCBr), 112173-16-7; $[Rh(3,5\text{-dmpz})(CO)_2]_2$, 33701-63-2; $[Rh(PZ)(CO)_2]_2$, 77244-11-2; $[Rh(3\text{-MPZ})(CO)_2]_2$, 99324-32-0; Na(3,5-dmpz), 41253-18-3; Rh, 7440-16-6.

Supplementary Material Available: Tables of hydrogen coordinates and thermal parameters (3 pages); a listing of observed and calculated structure factors (47 pages). Ordering information is given on any current masthead page.

Novel Chelating (N,O) Bis(carbene) Complexes of Chromium and Tungsten: Synthesis and Structure

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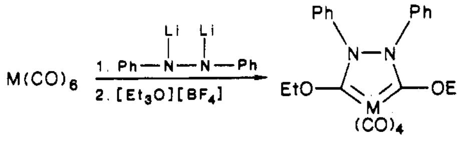
Addition of *N,N'*-dilithiohydrazobenzene to hexacarbonylchromium and -tungsten followed by alkylation affords tetracarbonyl complexes containing chelating bis(carbene) ligands that are characterized by spectroscopic means. A symmetrical planar metallocycle with slightly staggered phenyl substituents (dihedral angle = 49.4°) and a distorted octahedral coordination at the metal center is established by X-ray analysis for the chromium compound.

Introduction

The sequential addition of a nucleophile and an electrophile across the C–O bond of metal carbonyls represents the most versatile synthetic route to transition metal carbene complexes.[1] Recently, this methodology has been successfully extended to the addition of *vic* dianionic systems to homoleptic metal carbonyls.[2,3] This route provides a new entry to compounds containing chelating bis(carbene) ligands, a class of compounds of which only very few examples have been reported and characterized by reactivity and X-ray studies.[2–13] Interestingly, the compound regarded as the first isolated carbene complex[14] was of this type, but is was recognized as such only 55 years later.[15] In an effort to probe the general applicability of a chelating addition of nucleophiles to metal carbonyl systems, we have studied the reactivity of dimetalated hydrazines toward hexacarbonyl chromium and tungsten.

Results and Discussion

$Cr(CO)_6$ or $W(CO)_6$ reacts with *N,N'*-dilithiohydrazobenzene to give the chelating bis(acylmetalate) complexes that can be alkylated by $[Et_3O][BF_4]$ to give the alkoxyaminobis(carbene) chelates **1** and **2**. The new complexes are diamagnetic and air-sensitive. According to the N,O-heterosubstitution of the metal-coordinated carbene car-



1, M = Cr
2, M = W

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Table I. IR ν_{CO} (cm^{-1}) Spectra of Bis(carbene) Chelates 1-4[a]

1	2	3	4
2010 (m)	2020 (m)	2010 (m)	2030 (m)
1910 (vs)	1915 (vs)	1945 (vs)	1955 (vs)
1860 (s)	1860 (s)	1900 (s)	1900 (s)

[a] CH_2Cl_2.

Table II. ^{13}C NMR Data (ppm) for Bis(carbene) Chelates 1-4

	1[a]	2[a]	3[b]	4[a]
$C_{carbene}$	258.6	239.7	362.9	337.7
CO	230.5 (trans)	214.0 (trans)	235.6 (trans)	217.4 (trans)
	217.0 (cis)	198.6 (cis)	217.9 (cis)	201.5 (cis)
C_6H_5	137.6	137.6	140.1	139.4
	128.7, 128.1	128.8, 128.4	128.9, 128.6	128.6, 128.4
			127.0	126.9
OCH_2	72.9	74.9	78.7	80.6
CH			77.9	78.5
CH_3	15.2	15.2	14.9	14.8

[a] $CDCl_3$. [b] CD_2Cl_2.

Table III. ^1H NMR Spectra (δ) of Bis(carbene) Chelates 1-4

	1[a]	2[a]	3[b]	4[a]
C_6H_5	7.2 (m, 6 H)	7.3 (m, 6 H)	6.9 (m, 10 H)	1.0 (m, 10 H)
	6.9 (m, 4 H)	7.2 (m, 4 H)		
OCH_2	4.7 (q, 4 H)	4.8 (q, 4 H)	5.0 (q, 4 H)	4.6 (q, 4 H)
CH			4.1 (s, 2 H)	4.1 (s, 2 H)
CH_3	1.3 (t, 6 H)	1.4 (t, 6 H)	1.4 (t, 6 H)	1.6 (t, 6 H)

[a] $CDCl_3$. [b] CCl_4. [c] C_6D_6.

bon atom, the carbene ligand is a better donor compared with the alkoxybis(carbene) ligand in the isoelectronic $(CO)_4MC(OEt)CH(Ph)CH(Ph)C(OEt)$ (**3**, M = Cr; **4**, M = W) as demonstrated by the bathochromic shift of the ν_{CO} frequencies (Table I). The stabilizing effect of both heteroatoms on the carbene carbon in **1** and **2** is also evident from the ^{13}C NMR spectra. In comparison with its carbon analogues **3** and **4** the resonances for the carbene carbon atoms are shifted upfield by approximately 100 ppm. A similar effect can be observed in the pentacarbonyl carbene series $(CO)_5MC(OEt)X$ (M = Cr; X = NEt_2, Me).[16] The NMR spectra are summarized in Tables II and III.

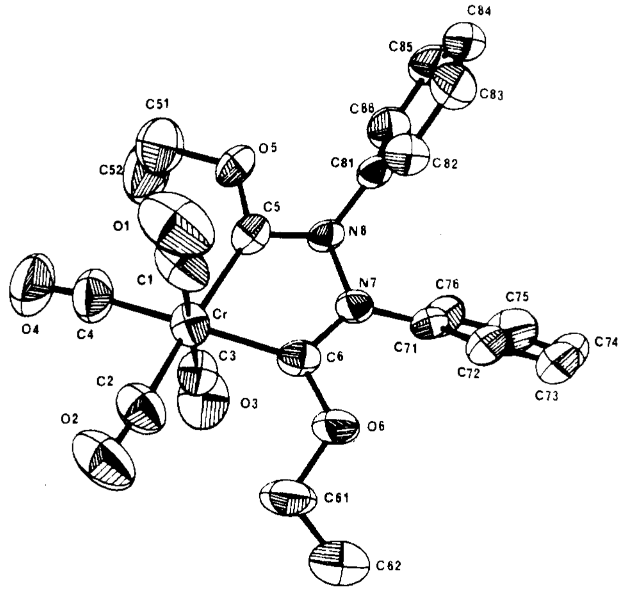

Figure 1. The molecular structure and labeling scheme for **1**. Selected bond lengths (Å) and angles (deg): Cr–C1, 1.858 (8); Cr–C2, 1.853 (7); Cr–C3, 1.877 (7); Cr–C4, 1.859 (7); Cr–C5, 2.024 (6); Cr–C6, 2.007 (5); C5–N8, 1.357 (8); C6–N7, 1.354 (7); N7–N8, 1.422 (7); C5–O5, 1.341 (9); C6–O6, 1.348 (8); C5–Cr–C6, 77.0 (2); Cr–C5–N8, 117.1 (4); C5–N8–N7, 113.7 (4); C6–N7–N8, 113.4 (4); Cr–C6–N7, 118.2 (4); C6–N7–C71, 126.7 (5); C71–N7–N8, 115.1 (4); C81–N8–N7, 115.3 (4); C5–N8–C81, 126.4 (5); Cr–C5–O5, 135.7 (4); O5–C5–N8, 105.7 (5); Cr–C6–O6, 135.8 (4); O6–C6–N7, 105.4 (5).

Table IV. Crystal and X-ray Collection Data for 1

formula	$C_{22}H_{20}CrN_2O_6$
cryst system	triclinic
space group	$P1$
a, Å	13.137 (6)
b, Å	9.55. (5)
c, Å	11.662 (6)
α, deg	125.66 (7)
β, deg	97.92 (6)
γ, deg	99.05 (6)
V, Å^3	1126
D(calcd), g cm^{-3}	1.36
Z	2
F(000)	476
μ(Mo Kα), cm^{-1}	5.31
unique reflctns	4962
reflctns with $I \geq 3\sigma(I)$	2729
R	0.073
R^w	0.066
cryst dimens, mm^3	0.5 × 0.4 × 0.3
takeoff angle, deg	6
scan type	$\omega/2\theta$
scan range, deg	2–28
scan speed, deg s^{-1}	0.04
linear absorp coeff (μ), cm^{-1}	5.31
remaining electron density, e	0.3

In order to establish the bonding properties of the chelating bis(carbene) ligand, especially in comparison with its carbon analogue in **3** and **4**, the crystal and molecular structure of **1** was established by X-ray analysis. A view of the compound is shown in Figure 1. The chelate ring adopts a twisted conformation in order to minimize the steric interaction of the two vicinal phenyl substituents.[3] As a consequence, the metal-coordinated carbene carbon atoms are inequivalent. In contrast, in the aza analogue **1** the CrC_2N_2 ring is (nearly) planar and has approximately C_{2v} symmetry. The presence of the additional heteroatom (N) at the carbene center induces only a minor lengthening of the metal–carbene bond whereas a remarkable change is reported for $Cr(CO)_5$ complexes bearing similarly substituted *monodentate* carbene ligands.[17] Despite the considerable double-bond character of the carbene nitrogen bond, the configuration at N7 and N8 deviates markedly from trigonal planar: the planes defined by N7, N8, C81 and C71, N7, N8, respectively, form a dihedral angle of 49.4°. This result may be rationalized again in terms of avoiding an eclipsed conformation of the phenyl rings at the expense of a less effective π-donation of the nitrogen atoms toward the carbene carbon atoms. Due to the geometry of the chelate ring the configuration at the metal center is distorted from octahedral. The small bond angle C5–Cr–C6 (77.0°) is compensated by an enlargement of

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Table V. Atomic Coordinates ($\times10^4$) with Esd's in Parentheses and Equivalent Isotropic Thermal Parameter, U_{eq} ($\times10^3$), for *cis*-$(CO_4)CrC(OEt)N(C_6H_5)N(C_6H_5)C(OEt)$

	x	y	z	U, Å^2
Cr	8674 (1)	6028 (1)	7638 (1)	62 (1)
C1	7777 (5)	5027 (8)	8240 (6)	79 (10)
O1	7234 (4)	4381 (6)	8596 (6)	137 (10)
C2	8586 (5)	8260 (8)	9160 (7)	82 (11)
O2	8560 (4)	9619 (6)	10178 (5)	119 (9)
C3	9611 (5)	6929 (8)	6986 (6)	74 (10)
O3	10176 (4)	7449 (7)	6561 (5)	122 (10)
C4	9870 (5)	6489 (9)	8997 (7)	93 (12)
O4	10620 (4)	6930 (7)	9901 (6)	141 (11)
C5	8457 (4)	3415 (7)	5941 (5)	62 (8)
O5	8806 (3)	2072 (5)	5760 (4)	81 (7)
C51	9690 (6)	2474 (10)	6909 (9)	125 (15)
C52	10664 (8)	3008 (13)	6677 (11)	176 (22)
C6	7496 (4)	5540 (6)	6045 (5)	59 (8)
O6	7038 (3)	6548 (4)	5808 (4)	76 (6)
C61	7397 (5)	8491 (7)	6964 (7)	96 (11)
C62	6999 (6)	9265 (9)	6312 (9)	128 (15)
N7	7099 (3)	3837 (5)	4767 (4)	52 (6)
C71	6570 (4)	3304 (6)	3341 (6)	57 (8)
C71	5502 (5)	3255 (7)	3034 (6)	76 (10)
C73	5004 (6)	2786 (9)	1684 (9)	100 (14)
C74	5538 (8)	2287 (9)	644 (8)	107 (14)
C75	6594 (7)	2314 (9)	939 (8)	114 (14)
C76	7116 (5)	2819 (8)	2313 (7)	84 (11)
N8	7617 (3)	2618 (5)	4731 (4)	52 (6)
C81	6975 (4)	768 (6)	3778 (5)	52 (7)
C82	5972 (4)	348 (7)	3905 (6)	68 (9)
C83	5365 (5)	−1449 (8)	3044 (6)	82 (10)
C84	5751 (6)	−2781 (8)	2072 (7)	84 (11)
C85	6751 (6)	−2347 (8)	1937 (6)	90 (11)
C86	7367 (4)	−572 (8)	2770 (6)	78 (10)

C4–Cr–C5 (101.4°) and C2–Cr–C6 (97.1°).

Experimental Section

All reactions and workup procedures were carried out in an atmosphere of purified and dried N_2. Solvents were dried by standard methods and distilled and stored under N_2. The silica gel used for column chromatography (silica gel 60, E. Merck, 0.06–0.20 mm) was dried at high vacuum and kept under N_2. The following instruments served for spectroscopic measurements: IR, Perkin-Elmer 399; ^1H NMR, ^{13}C NMR, Bruker WP.200.

$(CO)_4CrC(OEt)N(Ph)N(Ph)C(OEt)$ (1). $Cr(CO)_6$ (2.0 g, 9.1 mmol) was added to a stirred solution of PhN(Li)N(Li)Ph in 150 mL of Et_2O (6 mmol).[18] After 3 h the solvent was removed, the residue was dissolved in 20 mL of CH_2Cl_2 and 2 g (10.5 mmol) of $[Et_3O][BF_4]$ was added in small portions. The CH_2Cl_2 was evaporated off and the residue extracted into 150 mL of Et_2O. After evaporation of the ether, the product was chromatographed on silica gel at −10 °C with 7/3 pentane/CH_2Cl_2 as eluent and recrystallized from ether/pentane to give 0.45 g of 1 as pale orange microcrystals (yield ≃ 11%), mp 119 °C. Anal. Calcd for $C_{22}H_{20}CrN_{O6}$: C, 57.39; H, 4.34; Cr, 11.30; N, 6.08; O, 20.86. Found: C, 57.59; H, 4.37; Cr, 11.24; N, 5.92; O, 20.83.

$(CO)_4WC(OEt)N(Ph)N(Ph)C(OEt)$ (2). Compound **2** was prepared by the same method, starting with 3.50 g of $W(CO)_6$ (10 mmol). Dark yellow microcrystals of **2** (0.70 g, ≃ 12%) were obtained; mp 111 °C. Anal. Calcd for $C_{22}H_{20}N_2O_6W$: C, 44.60; H, 3.37; N, 4.73; O, 16.22; W, 31.06. Found: C, 44.46; H, 3.30; N, 4.54; O, 16.16; W, 30.89.

X-ray Structure Determination. Data were collected on a Philips PW 1100 four-circle automatic diffractometer equipped with a graphite monochromator. A total of 4962 independent reflections were collected, to which 2729 were considered as observed ($I \geq 3\sigma(I)$). Lorentz, Polarization, and empirical absorptions[19] were applied to correct the intensities. The structure was solved by analysis of the Patterson function and refined by a large-block least-squares method[20] with anisotropic factors for the non-hydrogen atoms to converge at R and R_w of 0.073 and 0.066, respectively. All H atoms appear on the difference Fourier map except for one on each of the methyl groups. They were placed therefore in idealized positions. Pertinent crystal and experimental parameters are given in Table IV. Atomic coordinates and equivalent isotropic thermal parameters are summarized in Table V.

Registry No. **1**, 112021-31-5; **2**, 112021-32-6; PhN(Li)N(Li)Ph, 23377-91-5.

Supplementary Material Available: Detailed bond lengths and angles (Table VI) (1 page); a listing of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

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