2978 *Inorg. Chem.* **1984**, *23*, 2978-2983

Contribution from the Institut für Anorganische Chemie, Johann Wolfgang Goethe-Universität,
D-6000 Frankfurt am Main 50, West Germany, and Departments of Chemistry, University of Houston,
Houston, Texas 77004, and Indiana University, Bloomington, Indiana 47405

Complex Chemistry of Reactive Organic Compounds. 46.[†1] Conformation of Metal Carbene Complexes: Synthesis and Structure of $(\eta^5\text{-}C_5H_5)Cr(CO)(NO)[C(C_6H_5)_2]$ and Its Relationship to the Isoelectronic Compound $(\eta^5\text{-}C_5H_5)Mn(CO)_2[C(C_6H_5)_2]$

WOLFGANG A. HERRMANN,*[2a,3] JOHN L. HUBBARD,[2a,4] IVAN BERNAL,[2b] JIM D. KORP,[2b]
BARRY L. HAYMORE,[2c,5] and GREGORY L. HILLHOUSE[2c,6]

Received December 9, 1983

Reaction of CpCr(CO)(NO)(thf) (Cp = η^5-C_5H_5, thf = tetrahydrofuran) with diphenyldiazomethane gives the new carbene complex $CpCr(CO)(NO)[C(C_6H_5)_2]$ (**2**). The complex crystallizes in the monoclinic space group $P2_1/n$ (a = 11.090 (2) Å, b = 10.579 (3) Å, c = 13.804 (3) Å, β = 92.43 (2)°). The structure shows the carbene plane to be nearly coplanar with the plane described by the N–Cr–C(carbene) fragment and nearly perpendicular to the C(carbonyl)–Cr–C(carbene) plane. In this orientation, the carbene ligand chooses to align itself with the most basic of the two potential π-donor orbitals of the CpCr(CO)(NO) fragment, e.g., the one *not* stabilized by the nitrosyl ligand. The resulting Cr–C(carbene) bond length of 1.912 Å is the shortest Cr–carbene distance yet reported. The structure of the isoelectronic compound $CpMn(CO)_2[C(C_6H_5)_2]$ (**4**) is reported for comparison. The manganese complex crystallizes in the space group $P2_1/c$ (a = 12.882 (2) Å, b = 7.380 (2) Å, c = 17.243 (2) Å, β = 106.95 (1)°). This latter structure sharply contrasts with that of the chromium derivative **2** in that the carbene plane is coincident with the mirror plane of the $CpMn(CO)_2$ fragment. Analysis of the room-temperature ^1H and ^{13}C NMR spectra of the two complexes shows the chromium–carbene conformation is locked whereas manganese–carbene rotation is fast.

Introduction

The conformations that unsaturated hydrocarbon ligands adopt in transition-metal complexes are of considerable interest with respect to understanding the fundamentals of metal—molecule activation. For carbene ligands the evaluation of subtle electronic factors, which help determine the geometries of mononuclear "Fischer-type" complexes containing the $(\eta^5\text{-}C_5H_5)Mn(CO)_2$- or $(\eta^6\text{-}C_6H_6)M(CO)_2$- fragments, has recently been addressed from theoretical[7] and experimental viewpoints.[8] At the heart of these discussions lies the matter of π bonding to the carbene carbon atom, both from the metal-containing moiety and from substituents on the carbene itself.

In this paper we report the synthesis and characterization of the (carbene)chromium complex $(\eta^5\text{-}C_5H_5)Cr(CO)(NO)[C(C_6H_5)_2]$ (**2**). This is the first example of a stable CO/NO carbene complex and provides an opportunity to examine the sensitivity of a carbene ligand to perturbations in orbital symmetry that are caused in going from $Mn(CO)_2^+$ to $Cr(CO)(NO)^+$ d^6 cores. A theoretical analysis of this perturbation was reported by Hoffmann et al.[9] in order to rationalize geometric asymmetry[10] and the stereochemical selectivity of nucleophilic addition to CpMo(CO)(NO)(η-allyl) cations reported by Faller et al.[11] Recent investigations by Gladysz et al. on the cationic species $[(\eta^5\text{-}C_5H_5)Re(NO)(PR_3)({=}CH_2)]^+$ have shown the sensitivity of the CH_2 ligand to orbital asymmetry caused by the Re(NO)(phosphine) core.[12] Our present report confirms the geometry predicted for a carbene ligand bound to a M(CO)(NO) core (d^6) by a single-crystal X-ray analysis of $(\eta^5\text{-}C_5H_5)Cr(CO)(NO)[C(C_6H_5)_2]$. We also include the X-ray analysis of the isoelectronic $(\eta^5\text{-}C_5H_5)Mn(CO)_2[C(C_6H_5)_2]$ complex, as well as a ^1H and ^{13}C NMR analysis for both complexes.

Experimental Section

All preparations described here were carried out under exclusion of air and moisture with use of standard Schlenk techniques. The diphenylcarbene–manganese complex **4** was synthesized according to published methods[13] and purified by column chromatography and subsequent crystallization at low temperature. For the generation of the thf complex $(\eta^5\text{-}C_5H_5)Cr(CO)(NO)(thf)$,[14] a 150-W mercury high-pressure lamp manufactured by the Original Quarzlampen GmbH Hanau was used (TQ 150). Any other light source of this type is suitable (e.g., Phillips HPK or Hanovia) for this preparation.

1. Preparation of Carbonyl(η^5-cyclopentadienyl)(diphenylcarbene)nitrosylchromium (2). The precursor complex $(\eta^5\text{-}C_5H_5)Cr(CO)_2NO$[15] was converted most efficiently to the thf derivative of composition $(\eta^5\text{-}C_5H_5)Cr(CO)(NO)(thf)$ by direct irradiation in thf solution using an immersion well apparatus (Pyrex glass; $\lambda > 290$ nm) equipped with an outer cooling jacket and a bottom gas inlet.[13b] During the irradiation, the solution was maintained at temperatures between −10 and −20 °C, and a slow stream of nitrogen was bubbled through the solution in order to prevent thermal decomposition and re-formation of the starting carbonyl complex. In a typical preparation, 0.75 g (3.7 mmol) of $(\eta^5\text{-}C_5H_5)Cr(CO)_2NO$ (A) in 230 mL of tetrahydrofuran was irradiated for 20 min. Approximately one-third of the chromium complex is converted to its thf derivative **1**. Diphenyldiazomethane[16] (0.35 g, 1.8 mmol) was then added to the

---

[†] Dedicated to Prof. E. O. Fischer on the occasion of his 65th birthday.

(1) Part 45: Herrmann, W. A.; Kriechbaum, G. W.; Steffl, I. *Z. Anorg. Allg. Chem.* **1984**, *508*, 100.
(2) (a) Johann Wolfgang Goethe-Universität. (b) University of Houston. (c) Indiana University.
(3) Karl Winnacker Fellow, 1979–1984.
(4) Alexander von Humboldt Fellow, 1983–1984.
(5) Present address: Monsanto Co., St. Louis, MO 63166.
(6) Present address: University of Chicago, Chicago, IL.
(7) (a) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 585. (b) Kostič, N. M.; Fenske, R. F. *J. Am. Chem. Soc.* **1982**, *104*, 3879.
(8) (a) Schubert, U. *J. Organomet. Chem.* **1980**, *185*, 373. (b) Schubert, U. *Organometallics* **1982**, *1*, 1085.
(9) Schilling, B. E. R.; Hoffmann, R.; Faller, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 592.
(10) (a) Faller, J. W.; Chodosh, D. F.; Katahira, D. *J. Organomet. Chem.* **1980**, *187*, 227. (b) Greenhough, T. J.; Legzdins, P.; Martin, D. T.; Trotter, J. *Inorg. Chem.* **1979**, *18*, 3268.
(11) Faller, J. W.; Shvo, Y. *J. Am. Chem. Soc.* **1980**, *102*, 5398.
(12) (a) Wong, W. K.; Tam, W.; Gladysz, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 5440. (b) Kiel, W. A.; Lin, G. Y.; Constable, A. G.; McCormick, F. B.; Strouse, C. E.; Eisenstein, O.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4865.
(13) (a) Herrmann, W. A.; *Chem. Ber.* **1975**, *108*, 486. (b) Fehlhammer, W. P.; Herrmann, W. A.; Öfele, K. "Handbuch der Präparativen Anorganischen Chemie", 3rd ed.; Brauer, G., Ed.; Enke Verlag: Stuttgart, West Germany, 1981; Vol. III, p 1799 ff.
(14) (a) Herberhold, M.; Alt, H. *Justus Liebigs Ann. Chem.* **1976**, 292. (b) Hames, B.; Legzdins, P.; Martin, D. T. *Inorg. Chem.* **1978**, *17*, 3644. (c) Herberhold, M.; Kremnitz, W.; Trampisch, H.; Hitam, R. B.; Rest, A. J.; Taylor, D. T. *J. Chem. Soc., Dalton Trans.* **1982**, 1261.
(15) Legzdins, P.; Malito, J. T. *Inorg. Chem.* **1975**, *14*, 1875.

0020-1669/84/1323-2978$01.50/0

Table I. Crystallographic Data of the Diphenylcarbene-Manganese Complex 4 and the Diphenylcarbene-Chromium Complex 2

	4	2
compd	$(\eta^5\text{-}C_5H_5)Mn(CO)_2[C(C_6H_5)_2]$	$(\eta^5\text{-}C_5H_5)Cr(CO)(NO)[C(C_6H_5)_2]$
formula	$C_{20}H_{15}MnO_2$	$C_{19}H_{15}CrNO_2$
fw	342.28	341.33
a, Å	12.882 (2)	11.090 (2)
b, Å	7.380 (2)	10.579 (3)
c, Å	17.243 (2)	13.804 (3)
β, deg	106.95 (1)	92.43 (2)
V, Å^3	1568	1618
Z	4	4
space group	$C_{2h}^5\text{-}P2_1/c$	$P2_1/n$
cryst	monoclinic prism, 0.21 × 0.22 × 0.35 mm	monoclinic prism, 0.20 × 0.20 × 0.30 mm
radiation	Mo Kα (λ = 0.710 69 Å) monochromatized with highly oriented graphite	Mo Kα (λ = 0.710 69 Å) monochromatized with highly oriented graphite
density, g cm^{-3}	1.450 (calcd, −160 °C), 1.41 (2) (exptl, 21 °C)	1.40 (calcd, 21 °C), 1.40 (exptl, 21 °C)
temp, °C	−160 (5)	21
μ, cm^{-1}	8.14	6.60
aperture	2.5 mm wide × 3.5 mm high; 22 cm from crystal	(5.20 + 2.11 tan θ) mm
takeoff angle, deg	2.0	2.0
scan speed, deg min^{-1}	3.0	0.5–4.0
scan width, deg	1.0 below Kα_1 to 1.2 above Kα_2	$\Delta\theta = (1.00 + 0.35 \tan\theta)$
bkgd counting	10 s	$^1/_4$ of scan time
2θ limits, deg	4–55	4–40
no. of variables	208	86
error in observn of unit wt	1.26	1.27
total unique data collected	4009	1523
unique data with $F_o^2 > 3\sigma(F_o^2)$	2937	740
$R(F)^a$	0.033	0.042
$R_w(F)^b$	0.046	0.032
wts	$w = 4F_o^2/\sigma^2(F_o^2)$	$w = \sigma(F)^{-2}$

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

mixture, which was subsequently stirred at 0 °C for 18 h. After removal of solvent in vacuo, the residue was chromatographed on 70–230 mesh silica (Merck 7734, activity grade II-III; column dimensions 1.2 × 60 cm, column temperature 15 °C). Elution with *n*-hexane/toluene (4:1) afforded unreacted A (0.20 g, 27%). $(\eta^5\text{-}C_5H_5)Cr(CO)(NO)[C(C_6H_5)_2]$ (**2**) was eluted as a bright red zone with a 1:1 *n*-hexane/toluene mixture, surrounded by yellowish traces of tetraphenylethylene. This latter impurity was removed by a second chromatography (Florisil 100–200 mesh, Merck 12999; column dimensions 1.2 × 60 cm, column temperature 15 °C). Here, elution with a 4:1 *n*-hexane/toluene mixture resulted in the organic impurity eluting first as a pale yellow zone, followed by the reddish chromium carbene complex **2**. Recrystallization from *n*-hexane at −35 °C gave 0.10 g (11%, based on consumed A) of crystalline $(\eta^5\text{-}C_5H_5)Cr(CO)(NO)[C(C_6H_5)_2]$ (**2**). The reddish orange crystals are stable in air for several days and dissolve in all comon organic solvents; mp 115–118 °C dec. Anal. Calcd for $C_{19}H_{15}CrNO_2$: C, 66.68; H, 4.43; N, 4.10; molecular weight, 341.33. Found: C, 66.76; H, 4.36; N, 4.12; molecular weight, 341 (EI mass spectrum, ^{52}Cr). Spectroscopic data: IR (cm^{-1}, *n*-hexane) 2000 (ν(CO)), 1690 (ν(NO)); ^{1}H NMR (270 MHz, acetone-d_6, TMS reference), $\delta(C_5H_5)$ 5.33 (s, 5 H), $\delta(C_6H_5)$ 6.7–7.3 (m, 10 H); ^{13}C NMR (67.88 MHz, CDCl$_3$, broad band decoupled, TMS reference): $\delta(C_5H_5)$ 97.0, $\delta(C_6H_5)$ 123.6, 125.9, 126.9, 127.2, 127.5, 128.5, 128.7, 157.8, 159.7, δ(CO) 225.2, δ(C(carbene)) 269.4.

2. Crystallographic Information. (a) The Manganese Complex $(\eta^5\text{-}C_5H_5)Mn(CO)_2[C(C_6H_5)_2]$ (4). X-ray data collection was accomplished by using a locally constructed diffractometer consisting of a Picker goniostat interfaced to a Texas Instruments TI980 computer. A liquid-nitrogen-cooled low-temperature device was used to maintain the low temperature. A well-formed crystal was mounted on the diffractometer, and monoclinic symmetry was determined. Subsequent data collection showed the space group to be $P2_1/c$. Background counts were measured at both ends of the scan with crystal and counter stationary. Intensities of 3 standard reflections were measured every 100 reflections and remained constant during the entire data collection. The intensity data were corrected for background effects and Lorentz–polarization effects. We determined that there was no need for an absorption correction, and a comparison of F_o and F_c in the final least-squares refinements showed no need for an extinction correction. Only reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in least-squares calculations. Values of $\sigma(F_o)$ were estimated by using a value of 0.05 for *p*. See Table I for pertinent crystal information and details of data collection.

The structure was solved by using a Patterson synthesis to locate the Mn atom, and subsequent difference Fourier syntheses revealed all remaining atoms including all 15 H atoms. The structure was refined with use of full-matrix least-squares techniques. During the refinements, the quantity minimized was $q = \sum w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure amplitudes and where w was taken to be $4F_o^2/\sigma^2(F_o^2)$. Atomic scattering factors were taken from the usual sources, and anomalous dispersion terms for Mn were included in F_c. The positions of the hydrogen atoms were idealized with C–H at 0.95 Å; their isotropic thermal parameters were chosen to be 1.0 Å^2 larger than the isotropic equivalents of the respective carbon atoms to which the H atoms were attached. The final structural model with 23 anisotropic atoms and 15 unrefined H atoms converged to $R(F) = \sum||F_o| - |F_c||/\sum|F_o| = 0.033$ and $R_w(F) = (q/\sum wF_o^2)^{1/2} = 0.046$. A statistical analysis of the trends of q as a function of observed structure amplitudes, diffractometer setting angles, and Miller indices showed nothing unusual and indicated that the weighting scheme was adequate. A final difference Fourier synthesis showed no significant residual electron density. Of the reflections with $3\sigma(F_o^2) > F_o^2$, only two had $F_o^2 > 4\sigma(F_o^2)$. Final positional parameters are shown in Table II. The pertinent structural data are given in Table IV. Thermal parameters and root-mean-square amplitudes are listed in Tables A, B, and C in the supplementary material.

(b) The Chromium Complex $(\eta^5\text{-}C_5H_5)Cr(CO)(NO)[C(C_6H_5)_2]$ (2). An Enraf-Nonius CAD-4 automatic diffractometer was used, with Mo Kα radiation monochromatized by a dense graphite crystal. Final cell constants as well as other information pertinent to data collection and refinement are listed in Table I. The Laue symmetry was determined to be $2/m$, and from the systematic absences noted the space group was unambiguously shown to be $P2_1/n$, an alternative setting of the conventional $P2_1/c$. Intensities were measured with use of the θ–2θ scan technique, with the scan rate depending on the net count obtained in rapid prescans of each reflection. In reduction of the data, Lorentz and polarization factors were applied, but no correction for absorption was made.

The structure was solved by direct methods, which provided the position of Cr and about half of the remaining atoms. The usual

---

(16) Staudinger, H.; Anthes, E.; Pfenninger, F. *Ber. Dtsch. Chem. Ges.* **1916**, *49*, 1928.

Table II. Positional Parameters of Dicarbonyl(η^5-cyclopentadienyl)(diphenylcarbene)manganese (4)[a]

atom	*x/a*	*y/b*	*z/c*
Mn	0.22940 (2)	0.27137 (4)	0.00131 (2)
C(1)	0.0863 (2)	0.3018 (3)	−0.04327 (13)
O(1)	−0.00525 (13)	0.3238 (2)	−0.07126 (10)
C(2)	0.2056 (2)	0.0834 (3)	0.05885 (12)
O(2)	0.19275 (13)	−0.0340 (2)	0.09906 (9)
C(3)	0.2401 (2)	0.5538 (3)	0.0393 (2)
C(4)	0.2830 (2)	0.4455 (4)	0.10726 (15)
C(5)	0.3724 (2)	0.3505 (3)	0.09567 (15)
C(6)	0.3856 (2)	0.4045 (3)	0.02174 (15)
C(7)	0.3036 (2)	0.5289 (3)	−0.01491 (14)
C(8)	0.23728 (15)	0.1275 (3)	−0.08712 (11)
C(11)	0.3225 (2)	0.1769 (3)	−0.12634 (12)
C(12)	0.3048 (2)	0.3169 (3)	−0.18290 (13)
C(13)	0.3870 (2)	0.3719 (3)	−0.21542 (15)
C(14)	0.4865 (2)	0.2873 (4)	−0.19222 (16)
C(15)	0.5043 (2)	0.1458 (4)	−0.13787 (15)
C(16)	0.4223 (2)	0.0881 (3)	−0.10553 (13)
C(21)	0.17092 (16)	−0.0300 (3)	−0.12643 (12)
C(22)	0.0819 (2)	−0.0954 (3)	−0.10288 (13)
C(23)	0.0207 (2)	−0.2421 (3)	−0.14156 (14)
C(24)	0.0455 (2)	−0.3289 (3)	−0.20509 (14)
C(25)	0.1322 (2)	−0.2668 (3)	−0.23057 (13)
C(26)	0.1935 (2)	−0.1210 (3)	−0.19215 (12)

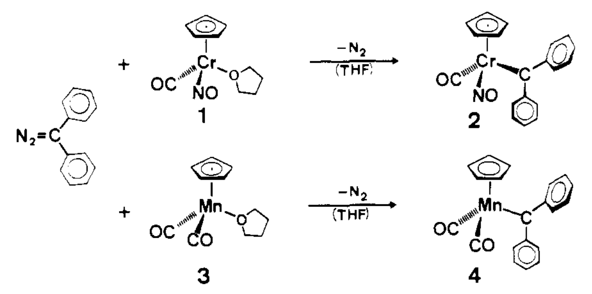
[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables.

Table III. Atomic Coordinates of Dicarbonyl(η^5-cyclopentadienyl)(diphenylcarbene)nitrosylchromium (2)

atom	*x/a*	*y/b*	*z/c*
Cr	0.1436 (1)	0.2511 (2)	0.8277 (1)
O(1)	0.4119 (5)	0.2539 (12)	0.7957 (5)
O(2)	0.1076 (6)	0.0380 (7)	0.7042 (5)
N	0.1264 (7)	0.1199 (7)	0.7611 (5)
C(1)	0.3100 (8)	0.2591 (16)	0.8055 (6)
C(2)	−0.0444 (4)	0.3240 (5)	0.8304 (4)
C(3)	0.0271 (4)	0.3935 (5)	0.8996 (4)
C(4)	0.1163 (4)	0.4602 (5)	0.8494 (4)
C(5)	0.1000 (4)	0.4321 (5)	0.7491 (4)
C(6)	0.0007 (4)	0.3479 (5)	0.7374 (4)
C(7)	0.1976 (7)	0.1815 (7)	0.9498 (6)
C(8)	0.2192 (5)	0.0444 (4)	0.9694 (4)
C(9)	0.3280 (5)	0.0075 (4)	1.0154 (4)
C(10)	0.3551 (5)	−0.1206 (4)	1.0266 (4)
C(11)	0.2733 (5)	−0.2118 (4)	0.9919 (4)
C(12)	0.1645 (5)	−0.1749 (4)	0.9459 (4)
C(13)	0.1375 (5)	−0.0468 (4)	0.9347 (4)
C(14)	0.2274 (5)	0.2622 (5)	1.0372 (3)
C(15)	0.3038 (5)	0.3666 (5)	1.0327 (3)
C(16)	0.3223 (5)	0.4444 (5)	1.1135 (3)
C(17)	0.2644 (5)	0.4177 (5)	1.1990 (3)
C(18)	0.1881 (5)	0.3133 (5)	1.2035 (3)
C(19)	0.1695 (5)	0.2356 (5)	1.1226 (3)
H(2)	−0.1142 (4)	0.2681 (5)	0.8446 (4)
H(3)	0.0164 (4)	0.3950 (5)	0.9712 (4)
H(4)	0.1794 (4)	0.5171 (5)	0.8794 (4)
H(5)	0.1497 (4)	0.4657 (5)	0.6961 (4)
H(6)	−0.0318 (4)	0.3118 (5)	0.6746 (4)
H(9)	0.3867 (5)	0.0729 (4)	1.0403 (4)
H(10)	0.4331 (5)	−0.1471 (4)	1.0596 (4)
H(11)	0.2927 (5)	−0.3036 (4)	0.9999 (4)
H(12)	0.1059 (5)	−0.2403 (4)	0.9210 (4)
H(13)	0.0595 (5)	−0.0203 (4)	0.9017 (4)
H(15)	0.3453 (5)	0.3857 (5)	0.9714 (3)
H(16)	0.3771 (5)	0.5192 (5)	1.1103 (3)
H(17)	0.2777 (5)	0.4734 (5)	1.2570 (3)
H(18)	0.1466 (5)	0.2942 (5)	1.2647 (3)
H(19)	0.1147 (5)	0.1607 (5)	1.1259 (3)

sequence of isotropic and anisotropic refinement was followed, after which all hydrogens were entered in ideally calculated positions. Since there were not too many observed data, the phenyl and cyclopentadienyl rings were subsequently fixed and refined as rigid bodies with ideal geometries and individual isotropic thermal parameters.

Scheme I



After all shift/esd ratios were less than 0.1, the refinement converged to the agreement factors listed in Table I. The only high correlations between variables in the final cycle of least squares involved the scale factor and the Cr thermal parameters. The atomic scattering factors for the non-hydrogen atoms were computed from numerical Hartree–Fock wave functions;[17] for hydrogen those of Stewart, Davidson, and Simpson were used.[18] The anomalous dispersion coefficients of Cromer and Liberman[19] were used for Cr. All calculations were made with the SHELX-76 series of programs.[20] Final positional and thermal parameters are shown in Table III, and the bonding geometry is detailed in Table V.

Results and Discussion

The ability of the chromium complex (η^5-C_5H_5)Cr(CO)(NO)(thf) to give a terminal carbene complex upon treatment with diazo reagents can be considered analogous to the chemistry previously shown for (η^5-C_5H_5)Mn$(CO)_2$(thf) (Scheme I).[13] The reaction of the photochemically and thermally sensitive (η^5-C_5H_5)Cr(CO)(NO)(thf) complex **1**, synthesized earlier by both Legzdins and Herberhold,[14] with diphenyldiazomethane at 0 °C in THF yields stable, red-orange, crystalline (η^5-C_5H_5)Cr(CO)(NO)[C$(C_6H_5)_2$] (**2**) in ca. 10% yield. The primary factor responsible for the low yield is the inefficiency in producing the labile tetrahydrofuran intermediate **2**, although gradual thermal degradation of the solvent complex alone at 0 °C can be observed by infrared spectroscopy.

Attempts to form the diphenylcarbene complex from reaction of the π-olefin complex (η^5-C_5H_5)Cr(CO)(NO)(η^2-cyclooctene)[14a] with diphenyldiazomethane failed, even at elevated temperatures. The reaction of (η^5-C_5H_5)Cr(CO)(NO)(thf) with diazomethane yields only (η^5-C_5H_5)Cr(CO)(NO)(η^2-C_2H_4), thus failing to give a μ-methylene complex analogous to (μ-CH_2)[(η^5-C_5H_5)Mn$(CO)_2]_2$ produced from the reaction of diazomethane with (η^5-C_5H_5)Mn$(CO)_2$(thf).[21]

Structure of Carbonyl(η^5-cyclopentadienyl)(diphenylcarbene)nitrosylchromium (2). The chromium–carbene complex has a distorted "piano stool" structure, where two of the legs are the carbonyl and nitrosyl ligands and the third leg is the diphenylcarbene ligand. The most interesting feature of the molecule is the relationship between the carbene plane, defined by C(8)–C(7)–C(14), and the carbonyl and nitrosyl ligands. The structure, shown in Figure 1, reveals the carbene plane to be nearly coplanar with the N–Cr–C(7) plane, the torsional angle N–Cr–C(7)–C(14) being 2.0°. This places the carbene plane in roughly a perpendicular orientation to the C(1)–Cr–C(7) plane, the C(1)–Cr–C(7)–C(14) torsional angle being 88.7°. Such geometry orients the carbene π-acceptor orbital to compete strictly with the carbonyl ligand and to be

---

[17] Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 321.

[18] Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

[19] Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

[20] Sheldrick, G. M. "SHELX-76 Programs for Crystal Structure Determination", Cambridge University: Cambridge, England, 1976.

[21] Herrmann, W. A.; Reiter, B.; Biersack, H. *J. Organomet. Chem.* **1975**, *97*, 245.

Table IV. Molecular Geometry of the Manganese–Carbene Complex 4

Intramolecular Bond Distances (Å)

Mn–C(1)	1.793 (2)	1.788 (av)	C(11)–C(12)	1.394 (3)	1.389 (av)
Mn–C(2)	1.783 (2)		C(12)–C(13)	1.396 (3)	
Mn–C(8)	1.885 (2)	2.172 (av)	C(13)–C(14)	1.375 (4)	
Mn–C(3)	2.177 (2)		C(14)–C(15)	1.377 (4)	
Mn–C(4)	2.175 (2)		C(15)–C(16)	1.397 (3)	
Mn–C(5)	2.153 (2)		C(16)–C(11)	1.394 (3)	
Mn–C(6)	2.173 (2)		C(21)–C(22)	1.408 (3)	1.396 (av)
Mn–C(7)	2.182 (2)	1.404 (av)	C(22)–C(23)	1.390 (3)	
C(3)–C(4)	1.393 (4)		C(23)–C(24)	1.384 (3)	
C(4)–C(5)	1.412 (4)		C(24)–C(25)	1.392 (3)	
C(5)–C(6)	1.392 (4)		C(25)–C(26)	1.384 (3)	
C(6)–C(7)	1.404 (4)		C(26)–C(21)	1.418 (3)	
C(7)–C(3)	1.421 (4)		C(1)–O(1)	1.148 (3)	1.148 (av)
C(8)–C(11)	1.492 (3)	1.488 (av)	C(2)–O(2)	1.148 (3)	
C(8)–C(21)	1.485 (3)				

Intramolecular Bond Angles (deg)

Mn–C(1)–O(1)	178.9 (2)	C(3)–Mn–C(5)	63.10 (10)	63.1 (av)
Mn–C(2)–O(2)	177.0 (2)	C(3)–Mn–C(6)	62.87 (9)	
Mn–C(8)–C(11)	116.7 (1)	C(4)–Mn–C(6)	62.92 (9)	
Mn–C(8)–C(21)	130.6 (1)	C(4)–Mn–C(7)	63.21 (9)	
C(11)–C(8)–C(21)	112.7 (2)	C(5)–Mn–C(7)	63.27 (9)	
C(1)–Mn–C(2)	90.80 (9)	C(3)–C(4)–C(5)	107.8 (2)	108.8 (av)
C(1)–Mn–C(8)	90.85 (9)	C(4)–C(5)–C(6)	108.1 (2)	
C(2)–Mn–C(8)	94.04 (9)	C(5)–C(6)–C(7)	108.8 (2)	
C(1)–Mn–C(3)	88.64 (9)	C(6)–C(7)–C(3)	106.9 (2)	
C(1)–Mn–C(4)	108.72 (10)	C(7)–C(3)–C(4)	108.5 (2)	
C(1)–Mn–C(5)	146.78 (10)	C(8)–C(11)–C(12)	120.4 (2)	121.2 (av)
C(1)–Mn–C(6)	143.19 (9)	C(8)–C(11)–C(16)	120.9 (2)	
C(1)–Mn–C(7)	105.67 (9)	C(8)–C(21)–C(22)	123.0 (2)	
C(2)–Mn–C(3)	125.70 (10)	C(8)–C(21)–C(26)	120.7 (2)	
C(2)–Mn–C(4)	93.22 (10)	C(11)–C(12)–C(13)	120.5 (2)	120.0 (av)
C(2)–Mn–C(5)	92.21 (9)	C(12)–C(13)–C(14)	120.2 (2)	
C(2)–Mn–C(6)	124.23 (10)	C(13)–C(14)–C(15)	119.9 (2)	
C(2)–Mn–C(7)	154.39 (9)	C(14)–C(15)–C(16)	120.5 (2)	
C(8)–Mn–C(3)	140.26 (10)	C(15)–C(16)–C(11)	120.1 (2)	
C(8)–Mn–C(4)	159.00 (9)	C(16)–C(11)–C(12)	118.6 (2)	
C(8)–Mn–C(5)	121.88 (10)	C(21)–C(22)–C(23)	121.6 (2)	120.0 (av)
C(8)–Mn–C(6)	96.89 (9)	C(22)–C(23)–C(24)	120.7 (2)	
C(8)–Mn–C(7)	104.96 (9)	C(23)–C(24)–C(25)	119.3 (2)	
C(3)–Mn–C(4)	37.33 (11)	C(24)–C(25)–C(26)	120.2 (2)	
C(4)–Mn–C(5)	38.08 (10)	C(25)–C(26)–C(21)	121.9 (2)	
C(5)–Mn–C(6)	37.54 (9)	C(26)–C(21)–C(22)	116.3 (2)	
C(6)–Mn–C(7)	37.60 (9)			
C(7)–Mn–C(3)	38.06 (9)			

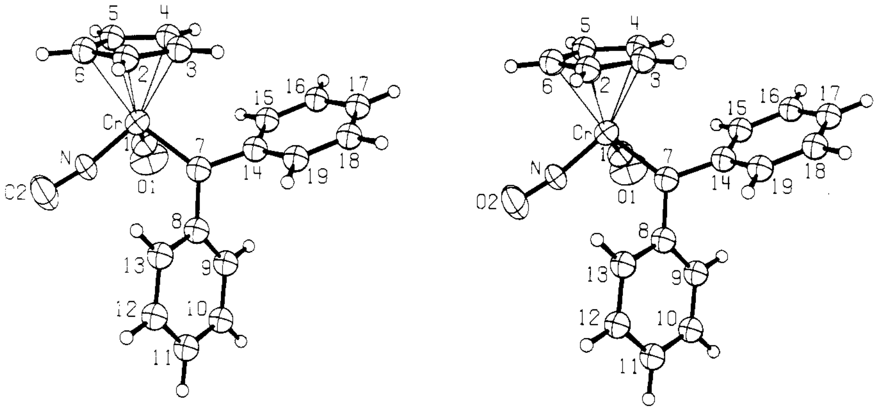


Figure 1. Stereoscopic view of the chromium–carbene complex 2 showing the atom-labeling scheme. The Cr, N, O, and C(1) atoms are 50% equiprobability envelopes, with the remainder shown as spheres of arbitrary diameter. The hydrogen atoms are numbered the same as the carbon atoms to which each is attached.

orthogonal to the strong π-accepting nitrosyl ligand.

The Cr–C(carbene) bond distance of 1.912 Å is the shortest chromium–carbene bond length yet reported and suggests that the observed carbene conformation favors a strong metal–carbene interaction. Previous work has shown the relationship between the π-donor ability of the metal-containing moiety and the length of the metal–carbene bond. Hence, the average Cr–carbene bond length for six-coordinate $(CO)_5CrL$-type complexes is 2.06 Å,[22] while the Cr–carbene bond length is 1.93 Å in the $(\eta^6\text{-}C_6H_6)Cr(CO)_2[C(OMe)(C_6H_5)]$ complex.[8a] Although not as short as a chromium–carbyne bond (1.74 Å),[23]

---

[22] (a) Dötz, K. H.; Füger-Köster, B.; Neugebauer, D. *J. Organomet. Chem.* **1979**, *182*, 489. (b) Kruger, G. J.; Coetzer, J.; Raubenheimer, H. G.; Lotz, S. *J. Organomet. Chem.* **1977**, *142*, 249. (c) Fischer, E. O.; Pardy, R. B. A.; Schubert, U. *J. Organomet. Chem.* **1979**, *181*, 37. (d) Fischer, E. O.; Held, W.; Kreissl, F. R.; Frank, A.; Huttner, G. *Chem. Ber.* **1977**, *110*, 656.

[23] Schubert, U. *Cryst. Struct. Commun.* **1980**, *9*, 383.

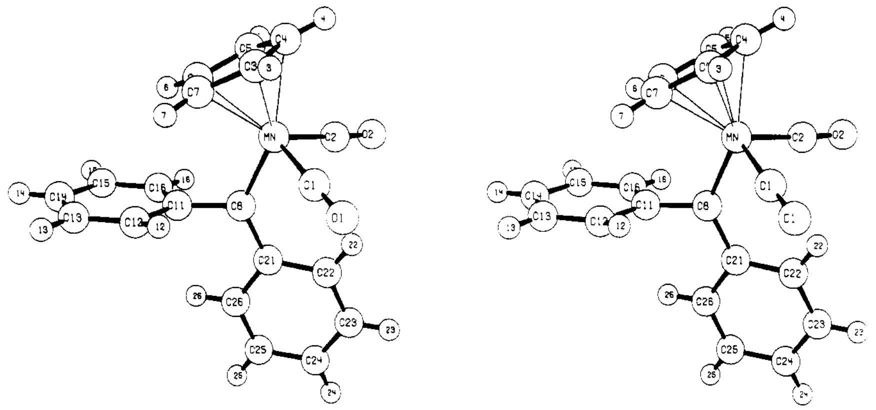


Figure 2. Stereoscopic view of the manganese–carbene complex **4** showing the numbering system employed in the crystallographic study. The atoms were all made isotropic and made of arbitrary size, convenient for representational purposes. Note that the plane of the phenyl ring defined by C(21–26) is nearly orthonormal to the plane of the phenyl ring defined by C(11–16) and that the plane of the former ring almost exactly bisects the angle C(1)–Mn–C(2). This is unlike the behavior of the isoelectronic chromium compound **2** depicted in Figure 1.

Table V. Molecular Geometry and Least-Squares Planes of the Chromium–Carbene Complex 2

Intramolecular Bond Distances (Å)

Cr-Cent[a]	1.884 (6)	Cr–C(6)	2.225 (6)
Cr-N	1.672 (8)	Cr–C(7)	1.912 (8)
Cr-C(1)	1.885 (9)	N-O(2)	1.182 (8)
Cr-C(2)	2.225 (5)	C(1)-O(1)	1.145 (8)
Cr–C(3)	2.243 (6)	C(7)–C(8)	1.493 (8)
Cr–C(4)	2.255 (6)	C(7)–C(14)	1.503 (8)
Cr–C(5)	2.243 (6)		

Intramolecular Bond Angles (deg)

N–Cr–Cent	122.8 (4)	Cr–N–O(2)	171 (1)
C(1)–Cr–Cent	123.0 (4)	Cr–C(1)–O(1)	174 (2)
C(7)–Cr–Cent	124.3 (4)	Cr–C(7)–C(8)	125.1 (5)
N–Cr–C(1)	92.1 (5)	Cr–C(7)–C(14)	122.6 (5)
N–Cr–C(7)	100.9 (4)	C(8)–C(7)–C(14)	112.2 (6)
C(1)–Cr–C(7)	83.6 (4)		

Torsion Angles (deg)

Cent–Cr–C(7)–C(8)	145.0	N–Cr–C(7)–C(8)	2.0
Cent–Cr–C(7)–C(14)	−37.2	Cr–C(7)–C(8)–C(9)	130.3
C(1)–Cr–C(7)–C(14)	88.7	Cr–C(7)–C(14)–C(19)	125.5

Least-Squares Planes and Deviations

plane	dev, (Å)	plane	dev, (Å)
(A) N, C(1), C(7)	0.99 (Cr)	(C) C(8). . .C(13)	0.13 (C(7))
(B) C(2). . .C(6)	−1.88 (Cr)	(D) C(14). . .C(19)	0.10 (C(7))

Dihedral Angles (deg)

A/B	4.5	A/C	103.1	A/D	23.1
B/C	101.0	B/D	18.6	C/D	94.9

[a] Cent is the Cp ring centroid.

the similarity of the chromium–carbene bond length of $(\eta^5\text{-}C_5H_5)Cr(CO)(NO)[C(C_6H_5)_2]$ to that of the above-mentioned η^6-benzene complex supports strong and similar π-donor capabilities of the $(\eta^5\text{-}C_5H_5)Cr(CO)(NO)$ and $(\eta^6\text{-}C_6H_6)Cr(CO)_2$ moieties.

The remaining structural features are quite typical of other similar complexes. The Cr–N–O angle of 171° shows only slight deviation from Cr–NO linearity, indicating a basically linear $[MNO]^6$ geometry in the scheme of Feltham and Enemark.[24] This is, however, slightly more than that found in $(\eta^5\text{-fluorenyl})Cr(CO)_2NO$,[25] an example where the absence of CO/NO disorder, so common to $(\eta^5\text{-}C_5R_5)M(CO)_2NO$ complexes (R = H,[25] CH_3[26]), allowed a determination of d^6 M–NO geometry. The carbonyl ligand is essentially linear, and the distances from the metal to the carbon atoms of the nearly planar π-cyclopentadienyl ring are essentially equal, averaging 2.238 Å. The C(7)–C(8) and C(7)–C(14) bond lengths along with the out-of-plane orientation of the phenyl rings with respect to the sp^2-carbene plane clearly show no type of phenyl conjugation toward the Cr–carbene bond. The carbene C(8)–C(7)–C(14) angle of 112° is comparable to that found in $(\eta^5\text{-}C_5H_5)Mn(CO)_2[C(C_6H_5)_2]$ (vide infra). The packing of the molecules in the unit cell (supplementary material) indicates no unusual intermolecular contacts.

Structural Description of Dicarbonyl(η^5-cyclopentadienyl)(diphenylcarbene)manganese (4). The solid-state structure contains discrete molecules of this complex with no unusual nonbonded intermolecular contacts. The molecule, shown in Figure 2, has the familiar tripod geometry, and Mn can be considered to have a pseudooctahedral coordination environment. The C_5H_5 ligand is planar within 0.009 Å, and the average C–C distance is 1.404 Å, which varies no more than ±0.015 Å around the ring. The Mn atom is located directly below the center of the C_5 ring 2.172 Å (average) away from the five carbon atoms. With the possible exception of Mn–C(5) (2.153 (2) Å), all Mn–C(cyclopentadienyl) distances are essentially the same; hence, there is no tilting or slippage of the C_5H_5 ligand. The two carbonyl ligands are linear (Mn–C–O = 178.0°) and have normal metric parameters (Mn–C = 1.788 Å, C–O = 1.148 Å). The carbene ligand has a Mn–C(8) distance of 1.885 (2) Å and is planar at the carbene carbon atom (C(8)); the Mn, C(8), C(11), and C(21) atoms are perfectly coplanar. The projection of the Mn–C(8) vector onto the cyclopentadienyl plane generates a line that passes through the center of the C_5 ring and is parallel to the C(3)–C(7) vector. The carbene ligand adopts the commonly observed orientation so that the plane of the carbene ligand bisects the C_5H_5 plane; the dihedral angle between the C_x–Mn–C(8) and Mn–C(8)–C(11)–C(21) planes is 3.4°, where C_x is the center of the C_5 ring.

Apart from the significantly improved precision of the present structure, it differs little from other manganese carbene structures within chemically and statistically allowable limits. A recent comparison of $CpMn(CO)_2(CX_2)$ structures bears this out.[8b] The plane of the lower C_6H_5 group (ring 2) bisects the C_5H_5 plane and is almost perpendicular to the plane of the upper C_6H_5 group (ring 1); the dihedral angle between the phenyl planes is 82.5°. The Mn–C(8)–C(11) angle is 116.7 (1)° and compares favorably with similar values in the range of 116–123° for CpMn(CO)$_2$(CXPh) (X = OEt, C(O)Ph, F). The Mn–C(8)–C(21) angle is 130.6°, which compares with values of 132–136° for the other carbenes. The

---

(24) Enemark, J. H.; Feltham, R. D. *Coord. Chem. Rev.* **1974**, *13*, 339.

(25) Atwood, J. L.; Shakir, R.; Malito, J. T.; Herberhold, M.; Kremnitz, W.; Bernhagen, W. P. E.; Alt, H. *J. Organomet. Chem.* **1979**, *165*, 65.

(26) Malito, J. T.; Shakir, R.; Atwood, J. L. *J. Chem. Soc., Dalton Trans.* **1980**, 1253.

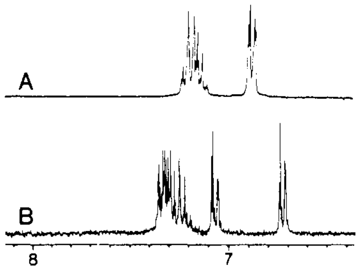


Figure 3. Room-temperature 270-MHz ^{1}H NMR spectra for (a) compound **4** and (b) compound **2**.

following dihedral angles for the carbene ligand in CpMn$(CO)_2(CPh_2)$ show its conformation to be normal: phenyl plane/carbene plane, 82.7° (phenyl 1), 2.6° (phenyl 2); phenyl plane/C_5H_5 plane, 28.5° (phenyl 1), 87.8° (phenyl 2); carbene plane/C_5H_5 plane, 86.8°.

NMR Study. The use of NMR spectroscopy for determining conformation and dynamics of the metal–carbene system is well established.[27] In particular, the results of previous NMR investigations on $(\eta^5\text{-}C_5H_5)Mn(CO)_2[C(CH_3)_2]$[28a] and $(\eta^5\text{-}C_5H_5)Mn(CO)_2[C(CH_3)(\eta^1\text{-}C_5H_5)]$[28b] show easy room-temperature rotation about the Mn–carbene bond, while X-ray results[29] show a solid-state carbene orientation like the present $(\eta^5\text{-}C_5H_5)Mn(CO)_2[C(C_6H_5)_2]$ structure. In addition to the typical singlet (5 H) from the $\eta^5\text{-}C_5H_5$ ligand, the 270-MHz ^{1}H NMR spectrum shows a phenyl region divided into two distinct parts with integration 6:4. Although lacking the simplicity of CH_2 or $C(CH_3)_2$ systems, these phenyl signals (Figure 3) can be interpreted as the ortho proton resonances appearing at slightly higher field from the meta and para protons; the two phenyl rings are made equivalent at room temperature by rapid Mn–carbene bond rotation. Rapid rotation about the Mn–carbene bond is also supported by the presence of only *one* ipso phenyl carbon resonance at 162.5 ppm in the ^{13}C NMR spectra.

Inspection of the ^{1}H NMR spectrum of the chromium complex **2** again shows a typical signal for the $\eta^5\text{-}C_5H_5$ ligand but a rather different phenyl region from that of the Mn complex **4**. In a manner similar to the above interpretation for the manganese complexes, the 6:2:2 integration can be interpreted as the six meta/para phenyl proton signals followed at higher field by two *different* groups of ortho phenyl proton signals. This evidence, together with the appearance of two *different* ipso phenyl ^{13}C NMR signals at 157.8 and 159.7 ppm, shows the diphenylcarbene ligand to not freely rotate about the Cr–carbene bond at room temperature.

The relatively large 83.4 ppm upfield shift of the ^{13}C NMR resonance from the manganese complex **4** to its isoelectronic chromium counterpart **2** is much larger than any other ^{13}C or ^{1}H shifts between the two complexes but parallels the ^{13}C shift for carbene carbon resonance found between $(\eta^5\text{-}C_5H_5)Fe(CO)[P(C_6H_5)_3](=CH_2)^+$[27] and $(\eta^5\text{-}C_5R_5)Re(NO)[P(C_6H_5)_3](CH_2)^+$.[12]

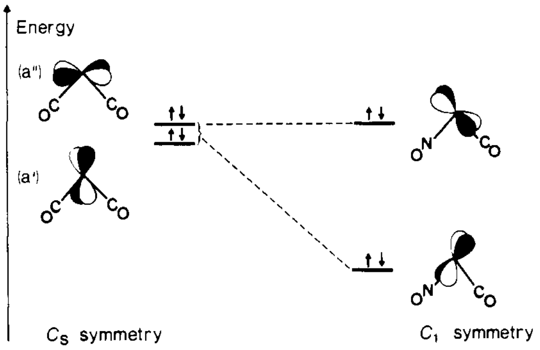


Figure 4. Qualitative correlation diagram for π-donor levels of the $Mn(CO)_2^+$ and $Cr(CO)(NO)^+$ fragments.

Electronic Structure Comparison. The most important result of this work is the experimental characterization of the electronic difference between the isoelectronic $(\eta^5\text{-}C_5H_5)Mn(CO)_2$ and $(\eta^5\text{-}C_5H_5)Cr(CO)(NO)$ moieties and the consequences on their bonding to carbene ligands. The previous work of Hoffmann et al.[9] discusses the orbital consequences of the $M(CO)_2$-to-$M'(CO)(NO)$ perturbation, and the reader is referred to this work for a detailed report. Briefly, the two donor levels from the $(\eta^5\text{-}C_5H_5)Mn(CO)_2$ moiety that are available for donation into the carbene π-acceptor orbital become energetically and spatially reoriented in the $(\eta^5\text{-}C_5H_5)Cr(CO)(NO)$ species (Figure 4). The orbital of the latter, which is directed toward the nitrosyl, is stabilized somewhat below that of the orbital oriented toward the carbonyl due to the stronger π-accepting power of NO. Thus, the best π-donor level of $(\eta^5\text{-}C_5H_5)Cr(CO)(NO)$ from both energetic and overlap viewpoints is the carbonyl-oriented level and forces the carbene ligand into the conformation we observe. The fact that the observed torsional angle N–Cr–C(7)–C(14) is ca. 2° shows that the rehybridization predicted from theory is nearly complete.

The carbene orientation in $(\eta^5\text{-}C_5H_5)Mn(CO)_2(CR_2)$ complexes has been argued from both overlap[7a] and energetic[7b] considerations. Both cases predict the carbene plane to lie in the $(\eta^5\text{-}C_5H_5)Mn(CO)_2$ mirror plane, but the perpendicular orientation is very close in energy. Hence, the barrier to metal–carbene bond rotation is fairly low in the manganese complex **4** but is quite high in the case of the nitrosylchromium complex **2**. Similar results for the $(\eta^5\text{-}C_5R_5)Re(NO)(PR_3)(CH_2)^+$ system have been reported by Gladysz et al.[12]

Acknowledgment. Generous support of this work has come from the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, the Welch Foundation, the National Science Foundation, and the Alexander von Humboldt-Stiftung.

Registry No. 1, 68013-61-6; **2**, 91295-96-4; **4**, 55971-21-6; A, 36312-04-6; $Ph_2C{=}N_2$, 883-40-9.

Supplementary Material Available: A list of calculated and observed structure factors of compound **4**, a stereoscopic view of the unit cell of compound **2**, and listings of thermal parameters and root-mean-square amplitudes of vibration of compound **4** and thermal parameters of compound **2** (19 pages). Ordering information is given on any current masthead page.

---

(27) (a) Brookhart, M.; Nelson, G. O. *J. Am. Chem. Soc.* **1977**, *99*, 6099. (b) Brookhart, M.; Tucker, J. R.; Flood, T. C.; Jensen, J. *J. Am. Chem. Soc.* **1980**, *102*, 1203.

(28) (a) Fischer, E. O.; Clough, R. L.; Besl, G. O.; Kreissl, F. R. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 543. (b) Fischer, E. O.; Besl, G. O. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1979**, *34B*, 1186.

(29) Fischer, E. O.; Friedrich, P.; Besl, G. O.; Huttner, G. *J. Organomet. Chem.* **1977**, *139*, C68–72.