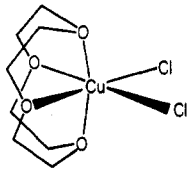
The ligands are staggered about the metal forming a regular square-antiprismatic coordination geometry. Views of the complex cation are shown in Figures 1 and 2. Selected bond distances and angles are given in Table II. The 12-crown-4 ligand has been found previously to form similar coordination polyhedra with Na^+ and Ca^{2+}. The $[Na(C_8H_{16}O_4)_2]X{\cdot}5H_2O$, X = Cl, OH, species have been examined structurally and shown to have square-antiprismatic coordination geometries.[8,9] In one case the metal ion was oriented along a twofold axis. For this reason space group *C*2 was given careful consideration in the present refinement. The calcium complex $[Ca(C_8H_{16}O_4)(H_2O)_4]Cl_2{\cdot}4H_2O$ has also been found to have a square-antiprismatic coordination geometry, consisting of one crown ether ligand and four aquo ligands.[10]

Unfortunately, the large standard deviations associated with the carbon and oxygen atom positions eliminate a detailed discussion of the specific features of the coordination geometry of $Mn(C_8H_{16}O_4)_2^{2+}$. The magnitude of these errors results from the combined effects of carbon atom disorder and the large contributions to the diffraction effect made by the heavy atoms. Nevertheless, the average Mn–O length of the structure shows clearly that the crown ether ligands are very weakly bound to the metal. This value of 2.31 Å is greater than 0.1 Å longer than Mn–O lengths in $Mn(H_2O)_6^{2+}$ which average to 2.18 Å.[11]

One other 12-crown-4 complex of a transition-metal ion has been characterized structurally. The $Cu(C_8H_{16}O_4)Cl_2$ molecule has been shown to have a distorted octahedral coordination geometry with cis chloro ligands (I).[12] In this structure



I

the flexibility and the steric constrains of the crown ether ligand are reflected in the trans O–Cu–O angle of 135.2 (1)°. The cis O–Cu–O angle is 84.2 (1)°. It is interesting to note in this structure the difference in Cu–O lengths at the two coordination positions. Values at the positions trans to the chloro ligands reflect relatively strong bonding (2.12 Å) compared with the trans Cu–O values (2.37 Å) and the values which we find for $Mn(C_8H_{16}O_4)_2^{2+}$. While crown ether coordination in $Mn(C_8H_6O_4)_2^{2+}$ is relatively weak, this need not be the case in all transition-metal complexes.

Structural features of the tribromide anions are quite regular with an average Br–Br length of 2.544 (7) Å and a linear bond angle of 179.2 (1)°.

Acknowledgment. Research carried out at the University of Colorado was supported under NIH Grant GM-23386. Research at Texas Tech University was supported by the Robert A. Welch Foundation under Grant D-531.

Registry No. $[Mn(C_8H_{16}O_4)_2](Br_3)_2$, 73017-46-6.

Supplementary Material Available: A listing of structure factor amplitudes (3 pages). Ordering information is given on any current masthead page.

(8) van Remoortere, F. P.; Boer, F. P. *Inorg. Chem.* **1974**, *13*, 2071.
(9) Boer, F. P.; Neuman, M. A.; van Remoortere, F. P.; Steiner, E. C. *Inorg. Chem.* **1974**, *13*, 2826.
(10) North, P. P.; Steiner, E. C.; van Remoortere, F. P.; Boer, F. P. *Acta Crystallogr., Sect. B* **1976**, *32*, 370.
(11) Carrell, H. L.; Glusker, J. P. *Acta Crystallogr., Sect. B* **1973**, *29*, 6389
(12) van Remoortere, F. P.; Boer, F. P.; Steiner, E. C. *Acta Crystallogr., Sect. B* **1975**, *31*, 1420.

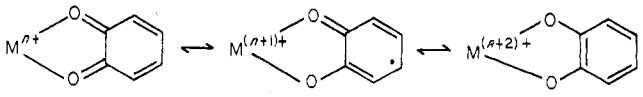
Contribution from the Departments of Chemistry, University of Colorado, Boulder, Colorado 80309, and the University della Calabria, 87030 Arcavacata (CS), Italy

Structural Features of $Ir(NO)(PPh_3)(O_2C_6Br_4)$, a Complex Molecule Containing both Quinone and Nitrosyl Ligands

William B. Shorthill,[1a] Robert M. Buchanan,[1a] Cortlandt G. Pierpont,*[1a] Mauro Ghedini,[1b] and Giuliano Dolcetti*[1b,c]

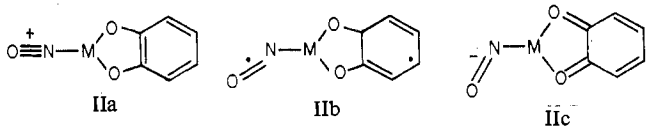
Received November 12, 1979

The ability of the nitrosyl ligand to bond with transition metals as either a one- or three-electron donor has been well established.[2] We have recently discussed the tautomeric forms of the *o*-quinone chelate ring which enable ligands of this type to alter charge at the metal center via intramolecular transfer of one or two electrons between the metal ion and the quinone π^* level (I).[3] Both ligands have demonstrated the property



I

of modulating charge at the metal center, and we have sought to exploit this feature catalytically by investigating a series of iridium complexes containing nitrosyl and quinone ligands.[4] In addition to regulating charge at the metal center the two types of ligands are capable of influencing their own modes of coordination intramolecularly. One can envision a series with members related by the transfer of electrons between the quinone and nitrosyl π^* levels (II). Through the series the



formal charge of the metal remains constant. Structural studies have played a central role in the characterization of both quinone and nitrosyl complexes. The structure of $Ir(NO)(PPh_3)(O_2C_6Br_4)$ has been determined crystallographically to characterize fully the modes of quinone and nitrosyl coordination in the $Ir(NO)(PPh_3)_2(Cat)$ complexes.

Experimental Section

A sample of $Ir(NO)(PPh_3)(O_2C_6Br_4)$, prepared by methods outlined previously,[4] was recrystallized from dichloromethane. Large prismatic crystals of the complex obtained by this procedure were found to contain one solvent molecule with the complex. Preliminary photographs indicated only triclinic symmetry, and space group $P\bar{1}$ was assumed. A crystal of dimensions 0.104 × 0.175 × 0.274 mm was mounted and aligned on a Syntex $P\bar{1}$ automated diffractometer. Lattice constants of a = 8.846 (1) Å, b = 15.848 (2) Å, c = 10.307 (2) Å, α = 87.68 (2)°, β = 93.12 (2)°, γ = 106.68 (2)°, and V = 1381.5 Å^3 were obtained from a least-squares refinement of the centered settings of 15 high-angle reflections. A calculated density of 2.145 g cm^{-3} agrees with an experimental value of 2.15 g cm^{-3} for two formula units of composition $Ir(NO)(P(C_6H_5)_3)(O_2C_6Br_4){\cdot}CH_2Cl_2$ per unit cell. Intensity data were collected within the angular range $3° \le 2\theta \le 50°$ by the θ–2θ scan technique using Mo Kα radiation.

(1) (a) University of Colorado. (b) Universita della Calabria. (c) Present address: Institute of Chemistry, Università di Udine, 33100 Udine, Italy.

(2) (a) Meyer, C. D.; Eisenberg, R. *Acc. Chem. Res.* **1975**, *8*, 26. (b) Enemark, J. H.; Feltham, R. D. *Coord. Chem. Rev.* **1974**, *13*, 339. (c) Frenz, B. A.; Ibers, J. A. *MTP Int. Rev. Sci.: Phys. Chem., Ser. One* **1972**, *11*, 33.
(3) Buchanan, R. M.; Fitzgerald, B. J.; Pierpont, C. G. *Inorg. Chem.* **1979**, *18*, 3439.
(4) Ghedini, M.; Denti, G.; Dolcetti, G. *Inorg. Chem.* **1978**, *17*, 2157.

 © 1980 American Chemical Society

Table I. Positional and Thermal Parameters for the Nongroup Atoms of $Ir(NO)(PPh_3)(O_2C_6Br_4)\cdot CH_2Cl_2$

atom	x	y	z	B_{11}[a]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ir	0.11538 (10)	−0.18371 (6)	0.07985 (9)	1.98 (4)	1.83 (4)	2.59 (4)	−0.03 (3)	−0.09 (3)	0.14 (3)
Br1	0.0432 (3)	−0.46080 (18)	0.33403 (25)	4.56 (13)	3.25 (14)	3.73 (13)	0.52 (11)	−0.71 (10)	1.18 (11)
Br2	−0.2064 (3)	0.37103 (18)	0.18349 (28)	4.56 (14)	2.58 (13)	5.50 (16)	−0.28 (11)	0.43 (12)	1.24 (12)
Br3	0.3936 (3)	−0.40824 (19)	0.07879 (28)	4.72 (14)	3.26 (14)	4.82 (15)	−1.28 (11)	−0.59 (11)	−0.65 (12)
Br4	0.2972 (3)	0.38956 (18)	0.20842 (25)	4.59 (13)	3.34 (14)	3.75 (13)	0.38 (11)	−1.59 (10)	−0.42 (11)
P	−0.2829 (6)	0.1150 (4)	−0.2442 (6)	1.93 (24)	2.08 (28)	3.3 (3)	−0.01 (21)	0.20 (21)	0.03 (23)
Cl1	−0.4328 (12)	0.3631 (8)	0.4547 (10)	10.0 (6)	10.0 (8)	7.3 (6)	4.1 (6)	0.1 (5)	0.3 (5)
Cl2	−0.6875 (13)	0.3953 (8)	0.5824 (12)	8.8 (7)	9.2 (8)	13.6 (9)	3.5 (6)	2.5 (6)	1.7 (7)
O1	−0.1729 (24)	0.0288 (14)	0.0842 (19)	8.5 (13)	4.6 (11)	5.3 (11)	0.7 (10)	−0.4 (9)	2.7 (10)
N	−0.1487 (20)	0.0920 (15)	0.043 (18)	2.6 (9)	5.3 (13)	2.6 (9)	1.1 (9)	−1.2 (7)	0.5 (9)
O2	0.0490 (17)	0.2622 (10)	0.0382 (14)	3.7 (7)	2.2 (8)	3.2 (7)	0.7 (6)	−0.4 (6)	0.3 (6)
O3	0.0838 (16)	−0.2914 (10)	0.1779 (13)	3.0 (7)	3.1 (8)	2.1 (7)	−0.8 (6)	−1.4 (5)	0.0 (6)
C1	0.0933 (24)	0.3442 (15)	−0.0100 (21)	2.4 (10)	2.3 (11)	2.9 (11)	1.0 (8)	0.1 (8)	1.2 (9)
C2	0.0238 (25)	0.3610 (16)	−0.1250 (20)	3.3 (11)	3.1 (12)	1.7 (10)	0.8 (9)	0.1 (8)	1.1 (9)
C3	0.0574 (26)	0.4450 (16)	−0.1761 (20)	3.2 (11)	2.9 (12)	2.0 (10)	0.9 (9)	0.6 (8)	0.2 (9)
C4	0.1668 (26)	0.5155 (15)	−0.1161 (22)	3.3 (11)	2.1 (11)	3.5 (12)	1.5 (9)	0.0 (9)	0.0 (10)
C5	0.2399 (25)	0.4987 (14)	−0.0027 (20)	3.5 (11)	1.5 (10)	2.1 (10)	0.1 (8)	0.1 (8)	0.6 (8)
C6	0.2054 (24)	0.4153 (17)	0.0539 (21)	1.9 (10)	3.9 (14)	2.8 (11)	0.6 (9)	−0.7 (8)	−1.3 (10)
C7	−0.4950 (36)	0.3876 (22)	0.5967 (30)	6.6 (18)	5.7 (20)	6.3 (18)	0.9 (15)	0.9 (15)	−1.7 (15)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. The quantities given in the table are in units of Å^2.

Table II

Derived Parameters for the Rigid-Group Atoms of $Ir(NO)(PPh_3)(O_2C_6Br_4)\cdot CH_2Cl_2$

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
R1C1	−0.6728 (18)	0.1895 (11)	−0.1659 (14)	4.0 (5)	R2C4	−0.2273 (12)	−0.0445 (10)	−0.1965 (15)	3.3 (5)
R1C2	−0.7545 (15)	0.1829 (13)	−0.2860 (17)	4.8 (6)	R2C5	−0.3429 (17)	−0.0021 (7)	−0.2263 (14)	2.5 (4)
R1C3	−0.6914 (19)	0.1579 (13)	−0.3939 (13)	5.6 (7)	R2C6	−0.5005 (15)	−0.0510 (10)	−0.2417 (15)	3.5 (5)
R1C4	−0.5466 (18)	0.1394 (12)	−0.3817 (12)	3.5 (5)	R3C1	−0.0913 (19)	0.0958 (10)	−0.5885 (14)	4.5 (6)
R1C5	−0.4649 (14)	0.1460 (11)	−0.2616 (15)	3.0 (5)	R3C2	−0.0448 (18)	0.1831 (11)	−0.6329 (12)	4.2 (6)
R1C6	−0.5280 (17)	0.1710 (11)	−0.1537 (11)	3.2 (5)	R3C3	−0.0725 (19)	0.2487 (8)	−0.5599 (15)	4.4 (6)
R2C1	−0.5426 (13)	−0.1424 (10)	−0.2273 (16)	4.3 (6)	R3C4	−0.1466 (19)	0.2270 (9)	−0.4424 (14)	3.6 (5)
R2C2	−0.4270 (19)	−0.1849 (7)	−0.1975 (16)	4.4 (6)	R3C5	−0.1931 (17)	0.1931 (17)	−0.3980 (12)	3.1 (5)
R2C3	−0.2694 (17)	−0.1359 (10)	−0.1822 (15)	3.6 (5)	R3C6	−0.1655 (18)	0.0741 (8)	−0.4710 (15)	3.3 (5)

Rigid-Group Parameters

group	x_c[a]	y_c	z_c	δ[b]	ϵ	η
R1	−0.6097 (12)	0.1644 (7)	−0.2738 (10)	2.86 (4)	1.810 (11)	−0.22 (4)
R2	−0.3849 (12)	−0.0935 (7)	−0.2119 (9)	−1.813 (9)	−2.991 (9)	0.119 (9)
R3	−0.1190 (11)	0.1614 (8)	−0.5154 (10)	−0.067 (10)	−3.022 (9)	−1.110 (10)

[a] x, y, and z are the fractional coordinates of the origin of the rigid group. [b] The rigid-group orientation angles δ, ϵ, and η (radians) have been defined previously: La Placa, S. J.; Ibers, J. A. *Acta Crystallogr.* **1965**, *18*, 511.

A scan rate of 4.0°/min was used. Data were corrected for Lorentz, polarization, and absorption effects (μ = 111.4 cm^{-1}). A total of 4986 reflections were found to have $F_o^2 > 3\sigma(F_o^2)$ and were included in the refinement. The structure was solved by the heavy-atom method and refined by using programs and procedures outlined previously.[5] Phosphine phenyl rings were refined as rigid groups. In final cycles of refinement the contributions from phenyl and dichloromethane hydrogen atoms were included as fixed corrections. Final discrepancy indices of R = 0.055 and R_w = 0.066 were obtained with the standard deviation of an observation of unit weight equal to 1.94. Final atomic positional and thermal parameters are given in Table I. Group atomic parameters are given in Table II. A listing of the final observed and calculated structure factor amplitudes (×10) is available as supplementary material.

Description of the Structure

A view of the $Ir(NO)(PPh_3)(O_2C_6Br_4)$ molecule is shown in Figure 1. Selected bond distances and angles are contained in Table III. The coordination geometry about the Ir atom is square planar with the quinone ligand chelated at two coordination sites. Carbon–oxygen lengths of the quinone ligand which average to 1.34 (2) Å are typical of chelated catecholate ligands.[3] The nitrosyl ligand has a linear Ir–N–O bond angle of 178 (2)°. These structural features are in accord with bonding structure IIa, and the metal is therefore Ir(I).

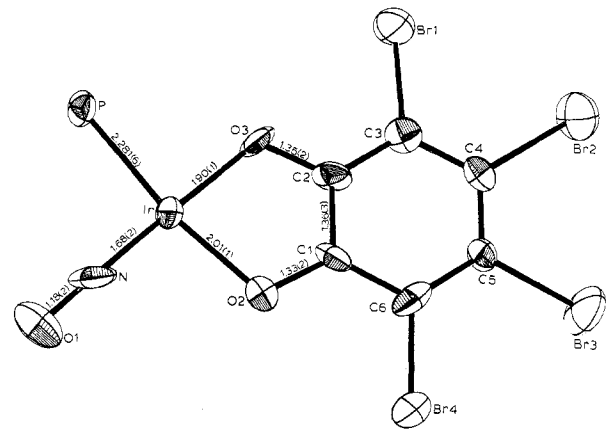


Figure 1. View of the $Ir(NO)(PPh_3)(O_2C_6Br_4)$ molecule showing the atom labeling scheme and the bond lengths within the inner coordination sphere.

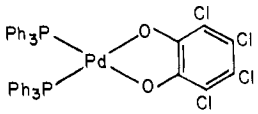
Previous studies have shown that catecholate ligands are quite effective donors. The complementarity of the strong π-acceptor ligands NO^+ and PPh_3 with the catecholate results in relatively short Ir–N and Ir–P lengths and an interesting pattern for the Ir–O lengths. Linear nitrosyl ligands have been found to have Ir–N lengths of 1.77 (1), 1.787 (8), and 1.67

(5) Pierpont, C. G. *Inorg. Chem.* **1977**, *16*, 636.

Table III. Bond Distances and Angles for the $Ir(NO)(PPh_3)(O_2C_6Br_4)$ Molecule

	Distances (Å)		
Ir–P	2.281 (6)	C3–C4	1.392 (30)
Ir–N	1.676 (22)	C4–C5	1.359 (28)
Ir–O2	2.008 (14)	C5–C6	1.381 (31)
Ir–O3	1.905 (14)	C6–C1	1.427 (30)
N–O1	1.186 (23)	C3–Br1	1.855 (22)
O2–C1	1.329 (24)	C4–Br2	1.845 (22)
O3–C2	1.345 (25)	C5–Br3	1.885 (21)
C1–C2	1.358 (28)	C6–Br4	1.833 (22)
C2–C3	1.367 (29)		
	Selected Angles (Deg)		
P–Ir–N	93.4 (6)	Ir–O2–C1	110.9 (13)
P–Ir–O2	168.8 (4)	Ir–O3–C2	114.9 (12)
P–Ir–O3	88.4 (4)	O2–C1–C2	117.6 (21)
N–Ir–O2	97.2 (7)	O2–C1–C6	123.8 (20)
N–Ir–O3	176.0 (8)	O3–C2–C1	115.3 (21)
O2–Ir–O3	81.2 (6)	O3–C2–C3	124.1 (19)
Ir–N–O1	177.8 (21)		

(2) Å for the Ir^- complexes $Ir(NO)_2(PPh_3)_2^+$, $Ir(NO)(CO)(PPh_3)_2$, and $Ir(NO)(PPh_3)_3$.[6-8] A length of 1.76 (2) Å was found for the Ir(0) complex $[Ir_2(NO)_2(PPh_3)_2]O$,[9] and a length of 1.68 (3) Å has been reported for the five-coordinate Ir(I) cation $Ir(H)(NO)(PPh_3)_3^+$.[10] The value of 1.676 (22) Å which we find for $Ir(NO)(PPh_3)(O_2C_6Br_4)$ is among the shortest lengths of this series. The Ir–P length of 2.281 (6) Å is also relatively short. Values found in the nitrosyl complexes above all exceed 2.31 Å and average to a length of 2.33 Å. Square-planar Ir(I) complexes with trans phosphine ligands also have values in this range.[11] The closely related palladium(II)–catecholate complex $Pd(PPh_3)(O_2C_6Cl_4)$ (III) has



III

Pd–P lengths which average to 2.286 (2) Å, a value which is nearly identical with the present length.[12] The Pd–O lengths of this structure are also closely related to the Ir–O length trans to the phosphine ligand. Palladium–oxygen lengths in this structure average to 2.033 (5) Å while the Ir–O2 length in the present case is 2.008 (14) Å. At the site trans to the nitrosyl ligand of $Ir(NO)(PPh_3)(O_2C_6Br_4)$ we find the Ir–O3 length to be 1.905 (14) Å, 0.10 Å *shorter* than the value for O2. This value is shorter than the Ir–O length of 1.941 (10) Å to the bridging oxo ligand of $[Ir_2(NO)_2(PPh_3)_2]O$ which is also located trans to a linear nitrosyl.[9]

The trend in Ir–O lengths found in this structure is contrary to what might be expected from the relative trans influences of the NO^+ and PPh_3 ligands. It can be understood if the catecholate ligand is viewed to be a strong π donor. Both the NO^+ and catecholate oxygens are strong σ donors, and the strong Ir–N bond would destabilize the trans Ir–O bond. The Ir–O3 length, however, appears anomalously short. As a strong π donor trans to the nitrosyl ligand, the synergistic bonding effect would serve to strengthen both the Ir–N and Ir–O3 bonds. There is indirect evidence for the π-donor strength of catecholate ligands in their molybdenum chemistry. They effectively replace oxo ligands from molybdenum, giving a series of oxygen deficient Mo(VI) complexes which are surprisingly inert to hydrolysis.[13] The oxo ligand is an effective π donor in its bonding with d^0 metals, and this property seems to also be true of the catecholates.

Acknowledgment. Research carried out at the University of Colorado was supported under NIH Grant GM-23386. Research at the University of Calabria was supported by the Italian CNR under Grant 7801013.03.

Registry No. $Ir(NO)(PPh_3)(O_2C_6Br_4)\cdot CH_2Cl_2$, 73178-92-4.

Supplementary Material Available: A listing of structure factor amplitudes (×10) (7 pages). Ordering information is given on any current masthead page.

(6) Mingos, D. M. P.; Ibers, J. A. *Inorg. Chem.* **1970**, *9*, 1105.
(7) Brock, C. P.; Ibers, J. A. *Inorg. Chem.* **1972**, *11*, 2812.
(8) Bombieri, G.; Forsellini, E.; Panattoni, C.; Graziani, R.; Bandoli, G. *J. Chem. Soc. A* **1970**, 1313.
(9) Carty, P.; Walker, A.; Mathew, M.; Palenik, G. *Chem. Commun.* **1969**, 1374.
(10) Mingos, D. M. P.; Ibers, J. A. *Inorg. Chem.* **1971**, *10*, 1479.
(11) Restivo, R.; Ferguson, G.; Kelly, T. L.; Senoff, C. V. *J. Organomet. Chem.* **1975**, *90*, 101.
(12) Pierpont, C. G.; Downs, H. H. *Inorg. Chem.* **1975**, *14*, 343.
(13) Buchanan, R. M.; Pierpont, C. G. *Inorg. Chem.* **1979**, *18*, 1616.

Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843

Theoretical Study of Vibrational Interaction Coordinates and π Bonding in Chromium Hexacarbonyl. Comparison with Cobalt Hexacyanide and Nickel Tetracarbonyl

David E. Sherwood, Jr., and Michael B. Hall*

Received July 13, 1979

Chromium hexacarbonyl has been extensively studied, both experimentally and theoretically, as a model system for transition-metal–carbon monoxide bonding. The near-zero-valent carbonyl complexes known suggest a synergistic effect, i.e., L → M σ donation balanced by M → L π acceptance. Values for these parameters are not readily accessible experimentally, and their magnitudes and relative importance are still being argued in the literature today.

Klemperer and Johnson have recently reported the results of scattered-wave Xα calculations (SW–Xα) for $Cr(CO)_6$.[1] Their results indicate that σ donation is the only important interaction for the metal–carbon bond and that the Cr 3dπ → CO 2π back-bonding strongly affects only the carbon–oxygen bonds. This is in direct conflict with earlier molecular orbital (MO) studies such as self-consistent charge and configuration (SCCC),[2] Hartree–Fock–Roothaan (HFR),[3] discreet variational Xα (DV–Xα),[4] and Fenske–Hall[5] MO calculations, which have been successfully used to interpret the ultraviolet adsorption spectrum[2] and low-energy photoelectron spectrum[3-5] of $Cr(CO)_6$, as has the more recent SW–Xα results. Unique to the SW–Xα study was its ability to rationalize the interaction coordinate analysis of the vibrational spectrum of $Cr(CO)_6$ by Jones et al.,[6] where it was shown that stretching a single metal–carbon bond ($Cr-C_0$, Figure 1) significantly affects only the trans metal–carbon bond ($Cr-C_t$). The cis metal–carbon bonds ($Cr-C_c$) are essentially unchanged. Although no attempt was made to calculate the interaction coordinates, this trans effect was used as confirmation of the SW–Xα σ-only bonding scheme. However, stretching the C_0–O_0 bond also causes changes in chromium–carbon bonding,

(1) Johnson, J. B.; Klemperer, W. G. *J. Am. Chem. Soc.* **1977**, *99*, 7132.
(2) Beach, N. A.; Gray, H. B. *J. Am. Chem. Soc.* **1968**, *90*, 5713.
(3) Hillier, I. H.; Saunders, V. R. *Mol. Phys.* **1971**, *22*, 1025.
(4) Baerends, E. J.; Ros, P. *Mol. Phys.* **1975**, *30*, 1735.
(5) Caulton, K. G.; Fenske, R. F. *Inorg. Chem.* **1968**, *7*, 1273.
(6) (a) Jones, L. H.; McDowell, R. S.; Goldblatt, M. *Inorg. Chem.* **1969**, *8*, 2349. (b) Jones, L. H. *J. Mol. Spectrosc.* **1970**, *36*, 398. (c) Jones, L. H. *Acc. Chem. Res.* **1976**, 128.

0020-1669/80/1319-1805$01.00/0 © 1980 American Chemical Society