Acknowledgment. This research was supported by grants from the National Institutes of Health (NS 07657) and the University of Wisconsin Graduate School.

(15) Predoctoral fellow of the National Institutes of Health (5 F01 GM 44429).

Marion H. O'Leary,* Gilbert A. Samberg[15]
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

Received March 5, 1971

A Novel Metal–Carbonyl–Metal Bonding System. Synthesis and Stereochemistry of $Al[W(CO)_3C_5H_5]_3(C_4H_8O)_3$

Sir:

We wish to report the synthesis, characterization, and stereochemistry of the transition metal carbonyl derivative $Al[W(CO)_3C_5H_5]_3(C_4H_8O)_3$ (**1**), the most stable member of a new series of group VIb complexes of the $Al(m)_3$ type; only one brief account of such a complex, $Al[Cr(CO)_3C_5H_5]_3$, has been reported.[1] Evidence from similar group III systems[2,3] suggests the possibility of metal–metal bonding,[4] and additional interest in these systems arises from some recently reported organoaluminum complexes of metal carbonyls in which the carbonyl ligands exhibit some unusual stereochemical[5] and spectroscopic[5–7] features.

The synthesis utilized the metal-exchange reaction previously employed for the convenient preparation of transition metal derivatives of zinc and cadmium;[8] at all stages, reactants and products were kept under an argon atmosphere. Solutions of **1** were prepared by stirring *ca.* 0.05 *M* solutions of $Hg[W(CO)_3C_5H_5]_2$ in tetrahydrofuran (THF) with excess powdered aluminum metal or powdered aluminum amalgam at room temperature for 15 min. The reaction was essentially quantitative; filtration yielded a light yellow, extremely air-sensitive solution of **1** which was used for subsequent reactions.[9]

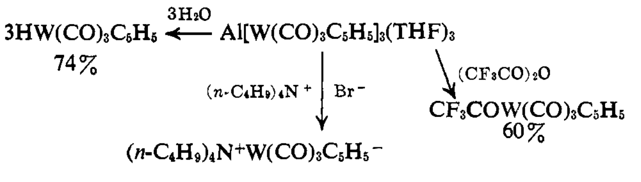
The infrared spectrum of **1** in THF and in the solid state were very similar (Table I) and exhibited some unusually low carbonyl stretching absorptions. In dimethylformamide (DMF), however, **1** appeared to be highly dissociated;[10] only the spectrum of $W(CO)_3C_5H_5^-$ was observed. Several reactions of **1** in THF (Scheme I) are characteristic of this anion; even though the ir data rule out its presence in significant concentration, it is readily available chemically, as indicated by its displacement by nucleophiles such as DMF and bromide ion,[11] and by its ready conversion to the hydride[12] or to the trifluoroacetyl derivative.[13]

Table I. Infrared Spectra of $Al[C_5H_5W(CO)_3]_3(THF)_3$ in the Carbonyl Stretching Region

Medium	Absorptions, cm^{-1} [a]
THF solution	1942 (0.9), 1854 (1.0), 1655 (0.2), 1591 (0.7), 1567 (0.6), 1548 (sh, 0.3)
DMF solution	1891 (0.9), 1773 (broad, 1.0)
Nujol mull	1934 (1.0), 1921 (0.9), 1850 (0.9), 1824 (1.0), 1670 (0.6), 1605 (0.8), 1570 (0.9)

[a] Relative intensities are given in parentheses.

Scheme I



Of particular interest are the carbonyl stretching absorptions of **1** in the 1540–1670-cm^{-1} region; at the time these observations were made, no precedent existed for such metal carbonyl absorptions other than the acyl–metal type.[14] The absorption band of $[C_5H_5Fe(CO)_2]_2 \cdot 2AlEt_3$ at 1682 cm^{-1} was attributed[5] to a bridging carbonyl also coordinated through oxygen to an aluminum atom. Infrared spectral data which further suggested the possibility of carbonyl oxygen coordination were reported for π-$Ph_3PC_5H_4Mo(CO)_3 \cdot AlMe_3$ (1665 cm^{-1})[6] and for n-$Bu_4N^+[W(CO)_3C_5H_5 \cdot AlPh_3]^-$ (1600 cm^{-1}).[7]

An X-ray diffraction analysis of **1** was undertaken on a nearly rectangular parallelepiped crystal (0.15 × 0.20 × 0.30 mm) sealed under argon in a thin-walled capillary tube. The diffraction symmetry was triclinic with $a = 11.419 \pm 0.003$, $b = 11.263 \pm 0.004$, $c = 16.156 \pm 0.006$ Å and $\alpha = 98.13 \pm 0.01$, $\beta = 100.55 \pm 0.01$, $\gamma = 100.23 \pm 0.01°$. Intensities were measured in a θ–2θ scan mode with Zr-filtered Mo Kα radiation on a Picker FACS-I diffractometer; of the 5589 independent reflections investigated ($\sin \theta/\lambda \leq 0.58$ Å^{-1}), a total of 4860 was statistically acceptable as observed data. The intensities were corrected for absorption and for Lorentz and polarization effects.

The coordinates of the three tungsten atoms were determined from a Patterson analysis based upon the space group $P\bar{1}$; all other atoms (excepting hydrogens) were located in two sequential Fourier syntheses. Block-diagonal least-squares refinement with anisotropic thermal parameters for all atoms (469 independent parameters) yielded a standard residual. $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$ of 0.077 was obtained for $w = 1/\sigma_{F^2}$. No attempt was made to locate hydrogen atoms.

---

(1) T. P. Whaley and V. Norman, U. S. Patent 3,071,493 (1963).

(2) D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, **5**, 1586 (1966).

(3) G. Schmid and H. Nöth, *J. Organometal. Chem.*, **7**, 129 (1967).

(4) For a review, see M. C. Baird, *Progr. Inorg. Chem.*, **9**, 1 (1968).

(5) N. J. Nelson, N. E. Kime, and D. F. Shriver, *J. Amer. Chem. Soc.*, **91**, 5173 (1969).

(6) J. C. Kotz and C. D. Turnipseed, *Chem. Commun.*, 41 (1970).

(7) J. M. Burlitch and R. B. Petersen, *J. Organometal. Chem.*, **24**, C65 (1970).

(8) J. M. Burlitch and A. Ferrari, *Inorg. Chem.*, **9**, 563 (1970).

(9) Addition of hexane to the THF solution precipitated **1** as a microcrystalline yellow powder which was sparingly soluble in toluene. All attempts to crystallize **1** from this solvent were unsuccessful. Crystals were obtained by slow diffusion of hexane into a saturated solution of **1** in 20% THF–toluene. This material did not melt below 280° under argon but decomposed slowly starting at 170°. Elemental analyses were satisfactory for metals but consistently low for C and H.

(10) J. M. Burlitch, *J. Amer. Chem. Soc.*, **91**, 4562 (1969).

(11) J. M. Burlitch, *ibid.*, **91**, 4563 (1969).

(12) Addition of the stoichiometric quantity of water to **1** in THF constitutes a convenient, high-yield synthesis of $HW(CO)_3C_5H_5$. Isolation is simply effected by evaporation of the solvent and sublimation of the residue.

(13) R. B. King and M. B. Bisnette, *J. Organometal. Chem.*, **2**, 15 (1964).

(14) For example, the acyl carbonyl band in $CF_3COW(CO)_3C_5H_5$ was observed at 1616 cm^{-1}; see ref 13.

The most striking and novel feature of the structure is the directly bonded sequence W–C–O–Al; the nearly regular octahedral stereochemistry around the aluminum atom involves three such linkages through one of the carbonyls on each of three [W(CO)$_3$C$_5$H$_5$] ligands (Figure 1). This is the first reported structure in which a CO ligand directly links two metal atoms through metal–carbon and metal–oxygen bonds. The O-coordination of a terminal carbonyl on the W(CO)$_3$C$_5$H$_5$ ligand provides an interesting contrast to the uniquely coordinated bridging carbonyl in [Fe(CO)C$_5$H$_5$COAlEt$_3$]$_2$ recently described by Nelson, Kime, and Shriver.[5]

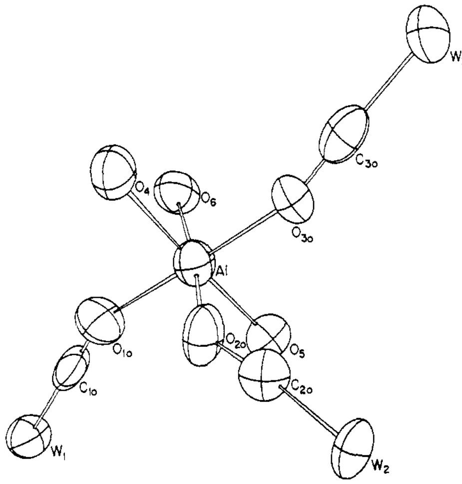


Figure 1. An ORTEP drawing of the central coordination about the aluminum atom in Al[W(CO)$_3$C$_4$H$_5$]$_3$(C$_4$H$_8$O)$_3$. THF oxygen atoms are designated O$_4$, O$_5$, and O$_6$. For clarity, the cyclopentadienyl groups, the terminal carbonyls, and the THF carbon atoms have been omitted.

The octahedral aluminum coordination is completed by three normal THF ligands in a mer configuration. The three [W(CO)$_3$C$_5$H$_5$] ligands display approximate mirror symmetry and are very nearly isostructural. The perpendicular distances of the three tungsten atoms to their respective π-C$_5$H$_5$ planes are identical (2.04 ± 0.01 Å) and, in each group, the cyclopentadienyl plane (with an average deviation from planarity of ±0.006 Å) is almost exactly parallel to the plane of the three carbonyl carbon atoms.

The W–C distances to the carbonyls (1.85 ± 0.02 Å) that link the tungsten atom to the central aluminum atom are systematically shorter than those to the terminal carbonyl groups (1.95 ± 0.02 Å). Conversely, the corresponding C–O distances are 1.25 ± 0.02 and 1.16 ± 0.02 Å, respectively.[15] The longer C–O bonds in the oxygen-coordinated carbonyls are presumably responsible for the unusually low carbonyl stretching frequencies observed for **1** (*vide supra*). The Al–O distances to the three carbonyls (1.827 ± 0.009 Å) are substantially shorter than those to the THF ligands (1.94 ± 0.02 Å). Thus a consistent picture of the W–C–O–Al sequence emerges, with rather tight bonding to the two metal atoms and with a somewhat extended C–O bond.

All of the W–C–O units are essentially linear (176° ± 3°) and all O–Al–O angles are orthogonal to within 3°. The Al–O–C angles, on the other hand, range from 140.4 to 162.9° and average 151°. It is probable that this spread reflects differing packing constraints at various points in the crystal.

In addition to the chromium and molybdenum analogs of **1**, we have prepared two similar series of compounds of the general formula L$_3$Al[(CO)$_3$MC$_5$H$_5$]$_3$ (M = Cr, Mo, W; L = pyridine, isoquinoline) through use of the stoichiometric quantity of L in toluene. Details of these derivatives and of the structure of **1** will be presented in forthcoming publications.[16]

---

[15] One terminal CO group in the cis ligand is exceptional in that the W–C and C–O bond distances are somewhat intermediate at 1.88 ± 0.02 and 1.24 ± 0.02 Å, respectively. All nonbonded contact distances are normal for this carbonyl and no metal–oxygen interactions are indicated.

(16) This work was supported by the National Science Foundation; the Alfred P. Sloan Foundation; the Petroleum Research Fund, administered by the American Chemical Society; and the Materials Science Center of Cornell University.

Robert B. Petersen, John J. Stezowski, Che'ng Wan
James M. Burlitch,* R. E. Hughes
Department of Chemistry, Cornell University
Ithaca, New York 14850
Received March 15, 1971

Electron Spin Resonance Evidence for Positive Holes Produced in Irradiated Single Crystals of Carboxylic Acids

Sir:

Although a number of esr studies have been made on irradiated single crystals of organic compounds, conclusive evidence for the positive hole has been obtained only for some sulfur-containing compounds such as thiourea derivatives, cystine hydrochloride, and dithiodiglycolic acid.[1] No conclusive evidence has been obtained for carboxylic acids, on which the most extensive work has been hitherto focused.

Recently, Iwasaki, Eda, and Toriyama found that irradiated single crystals of unsaturated carboxylic acids such as maleic acid[2] and potassium hydrogen maleate[3] give carboxyl radicals (RC(=O)O·) produced by the removal of an acidic proton, and suggested that the carboxyl radical could be formed from the positive hole by transferring H$^+$ to the neighboring molecule. Box, *et al.*, have also reported that a similar radical is formed in succinic acid.[1] The existence of this radical was assumed by some workers prior to our experimental evidence.[4,5]

However, the positive hole itself has never been found in irradiated carboxylic acids. Although the reason may be in the spontaneous transfer of an acidic proton from the positive hole, one may expect to find a similar carboxyl radical formed by ejection of an electron from the COO$^-$ group if salts of the carboxylic acids are used.

An example of the latter case has been found in the present study for one of the two kinds of carboxyl radicals formed in an irradiated single crystal of potassium hydrogen fumarate (KHF) or its deuterium compound (KDF), where an unpaired electron is located in the

---

(1) H. C. Box, H. G. Freund, K. T. Lilga, and E. E. Budzinski, *J. Phys. Chem.*, **74**, 41 (1970).

(2) M. Iwasaki, B. Eda, and K. Toriyama, *J. Amer. Chem. Soc.*, **92**, 3211 (1970).

(3) K. Toriyama and M. Iwasaki, *J. Chem. Phys.*, in press.

(4) R. N. Schwartz, M. W. Hanna, and B. L. Bales, *ibid.*, **51**, 4331 (1969).

(5) G. C. Moulton and B. Cernansky, *ibid.*, **53**, 3022 (1970).