potential energy *vs.* reaction coordinate graph, with the barrier to rearrangement being slightly higher than the energy difference between this structure and the ground structure.

Since the iron atom in $(\pi\text{-}C_5H_5)Fe(CO)_2$ has only one vacant σ orbital in its valence shell, the intermediate state in this process is consistent with the semiempirical rule which accords maximum stability to a 36-electron configuration for the metal atom in such compounds. In the 1,3 shift, on the other hand, the intermediate stage would involve a free C–C double bond and a bound π-allyl group, the latter having two more than the required number of electrons, with the least stable pair occupying a π-MO not symmetrically suited to overlap with the metal σ orbital.

It is interesting to compare the system studied here with the results recently reported by Fritz and Kreiter[25] for some cyclopentadienyl derivatives of the group four metals. In these cases the rate of the rearrangement process is so slow that it can only be observed in the form of a collapse of the σ-cyclopentadienyl spectrum to a single line at temperatures above room temperature for the silicon and germanium compounds, although for tetracyclopentadienyltin the process is rapid and only a single proton resonance line is observed even at −60°. These authors suggested a 1,2-shift mechanism, but no positive experimental evidence was offered to support this as against other possibilities such as those we have considered. The arguments presented here concerning $(\pi\text{-}C_5H_5)Fe(CO)_2C_5H_5$ can in principle be applied to these cases, but the data reported are insufficient actually to do so.

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[25] H. B. Fritz and C. G. Kreiter, *J. Organometal. Chem.*, **4**, 313 (1965).

Hydrogen Bridge Bonding in the $[M_2H(CO)_{10}]^-$ Anions (M = Cr, Mo, W)[1,2]

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Contribution from the Shell Development Comvany, Emeryville, California.

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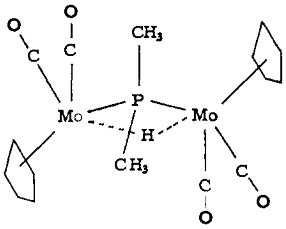
Abstract: Convenient syntheses have been developed for the $[M_2H(CO)_{10}]^-$ and $[M_2(CO)_{10}]^{2-}$ series of anions and the two series connected by an acid–base relationship. The formation of the mixed complexes $[MM'H(CO)_{10}]^-$ has been detected by proton nmr in statistically determined scrambling reactions involving pairs of the $[M_2H(CO)_{10}]^-$ anions, or pairs of the group VI metal hexacarbonyls. Infrared and proton nmr studies favor a symmetrical hydrogen-bridged structure for $[M_2H(CO)_{10}]^-$ in agreement with a recent X-ray structural investigation of $[(C_2H_5)_4N][Cr_2H(CO)_{10}]$.[17] The $[M_2(CO)_{10}]^{2-}$ series of complexes has been found to contain bridging carbonyl groups and is thus presumably isomeric with the complexes previously reported in the literature.[4,5]

Previous investigations of the anionic carbonyl complexes of the group VI metals have been carried out almost entirely by Behrens and his co-workers and, in a series of papers, they have reported the species $[M(CO)_5]^{2-}$,[3-5] $[MH(CO)_5]$,[3,4] $[M_2(CO)_{10}]^{2-}$,[4,5] $[M_2H(CO)_{10}]^-$,[4-6] and $[M_3(CO)_{14}]^{2-}$.[4,7] The structure of most of these anions, however, remains in doubt owing to the lack of spectroscopic and other physical data. In addition, many of the compounds were synthesized under unusual conditions (for example, in liquid ammonia at elevated temperatures) so that the complexes are not readily accessible for further study.

Our interest in the group VI carbonyl anions arose from a study of the complex $[(C_5H_5)_2Mo_2H(P(CH_3)_2)(CO)_4]$[8] which has recently been shown by Doedens and Dahl[9] to have structure **1**, although the position of the unique hydrogen was not detected by X-rays. The two molybdenum atoms have identical stereochemical environments, each possessing the "3-4" type of coordination previously found in $[C_5H_5Nb(CO)_4]$[10] and $[C_5H_5Mo(CO)_3]_2$.[11] In $[(C_5H_5)_2Mo_2H(P(CH_3)_2)(CO)_4]$, however, only three of the four basal coordination positions are occupied by ligands which are visible to X-rays, and it is presumed that a bridging hydride ligand occupies the fourth position, thus filling the vacant coordination site of both metal atoms. In such a complex, it is not clear whether or not the hydride ligand plays an important role in binding the two metal atoms together, owing to the simul-



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[1] Presented in part at the Second International Organometallic Symposium at Madison, Wis., Aug 29–Sept 3, 1965.

[2] Throughout this paper, M (or M′) = Cr, Mo, and W.

[3] H. Behrens and R. Weber, *Z. Anorg. Allgem. Chem.*, **291**, 123 (1957).

[4] H. Behrens and J. Vogl, *Chem. Ber.*, **96**, 2220 (1963).

[5] H. Behrens and W. Haag, *ibid.*, **94**, 312 (1961).

[6] H. Behrens and W. Klek, *Z. Anorg. Allgem. Chem.*, **292**, 151 (1957).

[7] H. Behrens and W. Haag, *Chem. Ber.*, **94**, 320 (1961).

[8] R. G. Hayter, *Inorg. Chem.*, **2**, 1031 (1963).

[9] R. J. Doedens and L. F. Dahl, *J. Am. Chem. Soc.*, **87**, 2576 (1965).

[10] H. W. Baird and L. F. Dahl, unpublished work quoted in ref 9.

[11] F. C. Wilson and D. P. Shoemaker, *J. Chem. Phys.*, **27**, 809 (1957).

Table I. Analytical Data for the Tetraethylammonium Salts of the $[M_2H(CO)_{10}]^-$ and $[M_2(CO)_{10}]^{2-}$ Anions

	% C		% H		% N		% O		% metal	
Anion	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd
$[Cr_2H(CO)_{10}]^-$	42.4	41.95	4.2	4.1	2.7	2.7	31	31.0	19.6	20.2
$[Mo_2H(CO)_{10}]^-$	32.9	35.8	3.4	3.5	2.2	2.3				
$[W_2H(CO)_{10}]^-$	27.9	27.75	2.7	2.7	1.8	1.8	19	20.5	46	47.2
$[Cr_2(CO)_{10}]^{2-}$	47.3	48.4	6.5	6.25	4.4	4.35	27.0[a]	24.8	15.8	16.1
$[Mo_2(CO)_{10}]^{2-}$	42.1	42.6	5.6	5.5	3.8	3.8	20.2	21.8	28.3[a]	26.2
$[W_2(CO)_{10}]^{2-}$	34.0	34.4	4.5	4.4	3.0	3.1	18.2	17.6	41.6	40.5

[a] By difference.

Table II. Infrared and Nuclear Magnetic Resonance Spectroscopic Data for the $[M_2H(CO)_{10}]^-$, $[MM'H(CO)_{10}]^-$, and $[M_2(CO)_{10}]^{2-}$ Anions

		ν_{CO}, cm^{-1}	
Anion	τ M–H[a]	Na$^+$ salt	Et$_4$N$^+$ salt
$[Cr_2H(CO)_{10}]^-$	29.17 (29.47)[b]	2032 (w), 1942 (vs), 1879 (s)[a]	2033 (w), 1943 (vs), 1881 (s)[e]
$[Mo_2H(CO)_{10}]^-$	22.15	2044 (w), 1946 (vs), 1881 (s)[a]	2035 (w), 1920 (vs), 1860 (s)[e]
$[W_2H(CO)_{10}]^-$	22.52 (22.60)[b]	2041 (w), 1941 (vs), 1879 (s)[a]	2043 (w), 1943 (vs), 1880 (s)[e]
$[CrMoH(CO)_{10}]^-$[a]	25.31	2030 (m), 2000 (w), 1930 (vs), 1870 (vs), 1830 (s)	. . .
$[MoWH(CO)_{10}]^-$[a]	22.37	2035 (w), 1930 (vs), 1875 (s)	. . .
$[CrWH(CO)_{10}]^-$[a]	25.43	2030 (w), 2010 (w), 1930 (vs), 1870 (vs), 1830 (s)	. . .
$[Cr_2(CO)_{10}]^{2-}$	. . .	1910 (sh), 1885 (vs), 1820 (m), 1810 (sh), 1740 (m)[c]	2050 (w), 1960 (m), 1930 (vs), 1870 (s), 1740 (m)[d]
$[Mo_2(CO)_{10}]^{2-}$	. . .	2035 (w), 2010 (w), 1930 (s), 1885 (vs), 1825 (s), 1800 (s), 1740 (s)[c]	2050 (w), 1980 (m), 1930 (sh), 1900 (sh), 1870 (vs), 1820 (s), 1770 (vs)[d]
$[W_2(CO)_{10}]^{2-}$	. . .	2020 (w), 1965 (sh), 1935 (s), 1890 (vs), 1825 (s), 1800 (s), 1740 (s)[c]	2010 (w), 1960 (sh), 1890 (vs), 1865 (sh), 1770 (s)[d]

[a] Data obtained from the tetrahydrofuran–sodium borohydride reaction mixtures. The data pertaining to the $[MM'H(CO)_{10}]^-$ anions were obtained from solutions also containing the corresponding pair of homobimetallic anions; all the observed infrared bands are recorded but only the hydride resonance assigned to the mixed species. [b] Tetraethylammonium salt in tetrahydrofuran. [c] Reaction mixture in tetrahydrofuran. [d] KBr disk. [e] Tetrahydrofuran solution.

taneous presence of the very strong dimethylphosphido bridging group. The situation is even more complex in the interesting compound $[Mn_3H(B_2H_6)(CO)_{10}]$[12] which not only contains hydrogen bridging two manganese atoms, but also a network of Mn–H–B bonds. The anion $[Fe_3H(CO)_{11}]^-$ [13] also appears to contain a bridging hydride ligand, as well as a bridging carbonyl group and iron–iron bonds.

In an attempt to resolve the ambiguity concerning the role of hydrogen in bridging two transition metals, we attempted to synthesize complexes in which no bridging ligands other than hydrogen would be present. Such a bonding situation had not previously been unambiguously characterized in transition metal chemistry.

Experimental Section

All manipulations were carried out under nitrogen using Schlenk tubes or in a nitrogen-filled drybox. The analytical data for the $[(C_2H_5)_4N][M_2H(CO)_{10}]$ and $[(C_2H_5)_4N]_2[M_2(CO)_{10}]$ complexes are given in Table I and infrared and proton nuclear magnetic resonance data in Table II.

Tetraethylammonium μ-Hydrido-bis(pentacarbonylchromium(0)). Chromium hexacarbonyl (5.0 g, 22.7 mmoles), sodium borohydride (0.50 g, 13.2 mmoles), and dry tetrahydrofuran were refluxed together until the characteristic infrared band due to the hexacarbonyl at 1975 cm^{-1} was no longer detected (about 18 hr). The reaction solution is initially colorless, but rapidly becomes orange and then gradually deepens to dark red. The final solution was filtered through degassed Celite Filteraid and the solvent removed under reduced pressure leaving an oily orange-red residue. Dry ethanol (*ca.* 100 ml) and a concentrated solution of tetraethylammonium bromide (2.4 g, 11.4 mmoles) in ethanol were added to the resulting solution. Precipitation of a yellow crystalline solid began at once and was completed by cooling overnight in a refrigerator. The product was filtered, washed with ethanol, and dried under vacuum, and was then analytically pure. The complex may be recrystallized from ethanol or tetrahydrofuran–hexane, preferably the latter as a slow decomposition appears to take place in ethanol giving a dark green crystalline product which was not identified.

The molybdenum and tungsten derivatives can be similarly prepared and require 4- and 18-hr reaction time, respectively. The final solution from $Mo(CO)_6$ is a very intense red, and the precipitated tetraethylammonium salt is purple. Recrystallization from tetrahydrofuran–hexane shows that this product consists mainly of soluble yellow $[Et_4N][Mo_2H(CO)_{10}]$ contaminated by a small amount of an unidentified, insoluble, intensely purple material. The tungsten complex is the most stable derivative of the three, does not give rise to any highly colored decomposition products, and can be crystallized from ethanol or handled in air for short periods without apparent harm. The yields of the pure complexes were in the range 65–85%.

The heterobimetallic hydrido carbonyl anions, $[MM'H(CO)_{10}]^-$, were prepared either by coreduction of equimolar mixtures of pairs of the group VI metal hexacarbonyls with sodium borohydride or by scrambling reactions between pairs of the $[M_2H(CO)_{10}]^-$ anions. The coreductions were carried out under the same conditions as described above, using a 16-hr reaction period. Scrambling reactions were carried out between equimolar quantities of the tetraethylammonium salts in concentrated tetrahydrofuran solutions in sealed nmr tubes. Both methods give a statistical mixture of anions and no attempt was made to separate the various species. The data given in Table II for $[MM'H(CO)_{10}]^-$ refers to measurements made on the unpurified reaction mixtures.

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(12) H. D. Kaesz, W. Fellmann, G. R. Wilkes, and L. F. Dahl, *J. Am. Chem. Soc.*, **87**, 2753 (1965).

(13) L. F. Dahl and J. F. Blount, *Inorg. Chem.*, **4**, 1373 (1965).

Ditetraethylammonium Di-μ-carbonyl-bis(tetracarbonylchromium-(−1)). Chromium hexacarbonyl (10 g, 40.5 mmoles) and sodium amalgam (3.15 g, 91 mmoles in 15 ml of mercury) in dry tetrahydrofuran (250 ml) were stirred and irradiated with ultraviolet light at room temperature. The solution slowly turned yellow, carbon monoxide was evolved, and new bands appeared in the carbonyl region of the infrared spectrum of the solution. After 12–18 hr, the reaction was essentially complete, as shown by cessation of gas evolution (1.2 moles of CO per mole of $Cr(CO)_6$) and the disappearance of the infrared band due to $Cr(CO)_6$. The solution was decanted from excess sodium amalgam and evaporated to dryness under reduced pressure leaving a crystalline yellow solid. Dry ethanol (100 ml) was added, the resultant solution filtered, and the filtrate treated with tetraethylammonium bromide (8.55 g, 40.5 mmoles) in ethanol (50 ml). The precipitated yellow solid was filtered, washed with ethanol, dried, and crystallized from acetone–ethanol or tetrahydrofuran–hexane. The complex is very air sensitive, rapidly turning green.

The analogous yellow molybdenum and tungsten complexes can be similarly prepared and were crystallized from acetone–ethanol. The tungsten complex is relatively stable to oxidation and can be handled in air without apparent detriment for short periods. The yields of the pure complexes were usually in the range 35–50%.

Reactions of the $[M_2(CO)_{10}]^{2-}$ Anions. Acid. $[(C_2H_5)_4N]_2[Cr_2(CO)_{10}]$ (1.48 g, 2.30 mmoles) was suspended in tetrahydrofuran and treated with a solution of HCl in ether (20 ml, 0.115 *N*). The complex slowly dissolved on stirring, and a white flocculent precipitate appeared. After 10 min, the infrared spectrum of the solution showed bands at 2025 (w), 1940 (vs), and 1880 (m). Filtration and evaporation gave pure $[(C_2H_5)_4N][Cr_2H(CO)_{10}]$ (nmr spectrum in THF showed a singlet at τ 29.4).

Anal. Calcd for $C_{18}H_{21}Cr_2NO_{10}$: C, 42.0; H, 4.1. Found: C, 41.7; H, 4.3.

$[(C_2H_5)_4N]_2[W_2(CO)_{10}]$ (3.54 g, 3.90 mmoles) was dissolved in dry acetone and treated with HCl in ether (34 ml, 0.115 *N*) to give an immediate white precipitate of $[(C_2H_5)_4N]Cl$. The soluble product was isolated as above and identified by its infrared and nmr spectra in solution and by analysis.

Anal. Calcd for $C_{18}H_{21}NO_{10}W_2$: C, 27.75; H, 2.7. Found: C, 27.8; H, 2.8.

The reaction of $[(C_2H_5)_4N]_2[W_2(CO)_{10}]$ with acid (Figure 5) and the reverse reaction of $[Et_4N][Mo_2H(CO)_{10}]$ with base have also been followed by means of the infrared spectrum of the carbonyl region. Excess acid has no apparent effect on the spectrum of $[W_2H(CO)_{10}]^-$ so that further protonation to give a neutral species does not occur under these conditions.

Perfluoropropyl Iodide. $Na_2[Cr_2(CO)_{10}]$ (5.5 mmoles) in tetrahydrofuran was treated with C_3F_7I (26.6 g, 11 mmoles) to give an immediate color change from yellow to red. Evaporation of the solvent left an oily red hydrocarbon-insoluble residue. Addition of acetone gave a red solution which, when treated with ethanolic $[Ni(phen)_3]Cl_2$, gave orange crystals on standing. Recrystallization from dichloromethane–hexane gave needles identical with a specimen of $[Ni(phen)_3][CrI(CO)_5]_2$ prepared from $[CrI(CO)_5]^-$ which was obtained by the method of Abel.[14]

Anal. Calcd for $C_{46}H_{24}Cr_2I_2N_6NiO_{10}$: C, 44.6; H, 2.0; I, 17.5; N, 6.8; Ni, 4.8; O, 12.9. Found: C, 44.8; H, 2.2; I, 17.5; N, 6.7; Ni, 4.8; O, 11.2.

Mercuric Chloride. An ethanolic solution of $Na_2[Mo_2(CO)_{10}]$ was treated with excess ethanolic mercuric chloride to give an immediate grayish precipitate which was identified as mercurous chloride. The only carbonyl species remaining in solution was identified as $Mo(CO)_6$ by infrared spectroscopy.

$[Ni(phen)_3]^{2+}$. Ethanolic solutions of approximately equimolar quantities of $Na_2[Mo_2(CO)_{10}]$ and $[Ni(phen)_3]Cl_2$ gave, on mixing, a dark brown precipitate. Crystallization from acetone and then dichloromethane gave dark red shining crystals of $[Mo(phen)(CO)_4]$ which were identified by analysis and by comparison with an authentic specimen prepared from $Mo(CO)_6$ and phenanthroline in diglyme.

Anal. Calcd for $C_{16}H_8MoN_2O_4$: C, 49.5; H, 2.1; Mo, 24.7; N, 7.2; O, 16.5. Found: C, 49.4; H, 2.2; Mo, 25; N, 6.7; Ni, 0.03; O, 15.7.

Attempts were also made to prepare anionic derivatives of tertiary phosphine substituted metal hexacarbonyls. For example, $[Mo(CO)_5P(C_6H_5)_3]$ was reduced with sodium amalgam with irradiation as described above to give a red tetrahydrofuran solution. Evaporation of the solution and extraction of the residue into ethanol gave pale yellow insoluble $[Mo(CO)_4(P(C_6H_5)_3)_2]$ and a red solution containing $Na_2[Mo_2(CO)_{10}]$, both identifications being by infrared spectroscopy.

Conductivity Behavior of $[(C_2H_5)_4N]_2[W_2(CO)_{10}]$ and $[(C_2H_5)_4N][W_2H(CO)_{10}]$. The conductance of nitromethane solutions of the two salts was measured at room temperature (26°) over a concentration range of $3\text{–}50 \times 10^{-4}$ equiv/l. using an ESI Universal Impedance Bridge, Model 250DA.

A nonlinear relationship between Λ_c and $c^{1/2}$ was found for $[(C_2H_5)_4N]_2[W_2(CO)_{10}]$ so that an accurate value for Λ_0 could not be found although the approximate value (105 mho cm^2 equiv^{-1}) is consistent with the behavior of a 2:1 electrolyte. The conductance data of $[(C_2H_5)_4N][W_2H(CO)_{10}]$, however, could be described by an expression of the type $\Lambda_0 - \Lambda_c = Bc^{1/2}$, where the Λ_0 and B values (91.9 mho cm^2 equiv^{-1} and 187, respectively) are in the range expected for a 1:1 electrolyte.[15]

Results

The $[M_2H(CO)_{10}]$ Anions. This investigation has shown that the reaction of the group VI metal hexacarbonyls with sodium borohydride in tetrahydrofuran yields the anionic complexes $[M_2H(CO)_{10}]^-$ as the major products. The reaction probably occurs according to eq 1.

$$2Cr(CO)_6 + NaBH_4 \longrightarrow Na[Cr_2H(CO)_{10}] + 2CO + [BH_3] \quad (1)$$

The borine fragment presumably remains in solution as a tetrahydrofuran complex and has not been identified. Our results are thus at variance with those of Behrens, *et al.*,[4,7] although they are in agreement with the recent independent studies of Graham.[16] The reason for the discrepancy is not immediately obvious, although we have observed certain minor highly colored reaction products in some of the reactions, particularly those of chromium and molybdenum. It is possible that, under experimental conditions not yet clearly defined, these become dominant and may prove to be identical with $[M_3(CO)_{14}]^{2-}$.[4,7]

The observed reaction products are however apparently identical with the $[M_2H(CO)_{10}]^-$ complexes prepared earlier by Behrens either by hydrolysis of $[M_2(CO)_{10}]^{2-}$[4,5] or oxidation of $[M(CO)_5]^{2-}$ with aqueous ammonia solution.[3,4] A direct comparison of the $[M_2H(CO)_{10}]^-$ complexes prepared by these methods with the corresponding series presently under discussion has not as yet been possible owing to the lack of available spectroscopic or other physical data for the earlier series of complexes. Both methods however give yellow complexes of similar solubility characteristics.

Prior to the determination of the structure of $[(C_2H_5)_4N][Cr_2H(CO)_{10}]$ by X-ray crystallography,[17] we had assigned a structure essentially equivalent to **2** to this complex and to the others in the series. The evidence on which this conclusion was based is discussed below.

The reaction of the group VI metal hexacarbonyls with sodium borohydride in tetrahydrofuran is conveniently followed by means of the infrared spectra of the reaction solutions. As the reaction proceeds, the strong band at about 1970 cm^{-1} due to $M(CO)_6$ weakens and a group of three new bands appear until, when reaction is complete, the spectra resemble Figure 1.

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[14] E. W. Abel, I. S. Butler, and J. G. Reid, *J. Chem. Soc.*, 2068 (1963).

[15] R. D. Feltham and R. G. Hayter, *ibid.*, 4587 (1964).

[16] U. Anders and W. A. G. Graham, *Chem. Commun.*, 499 (1965).

[17] L. B. Handy, P. M. Treichel, L. F. Dahl, and R. G. Hayter, *J. Am. Chem. Soc.*, **88**, 336 (1966).

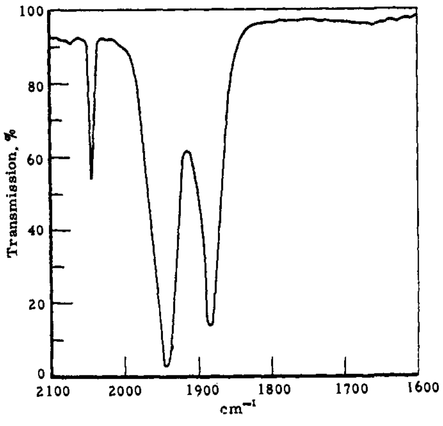


Figure 1. Infrared spectrum of $[(C_2H_5)_4N][W_2H(CO)_{10}]$ in carbonyl region (THF solution).

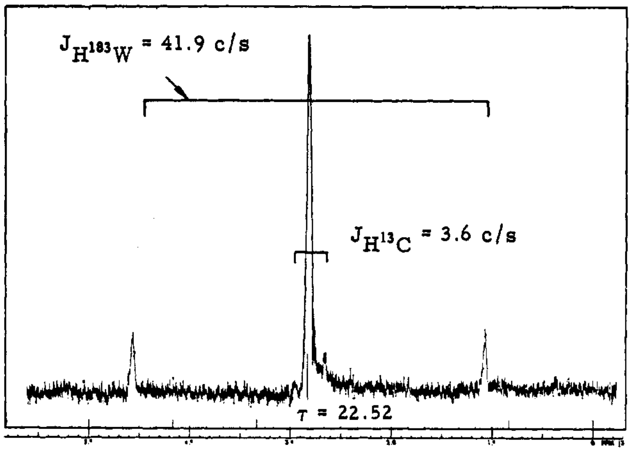
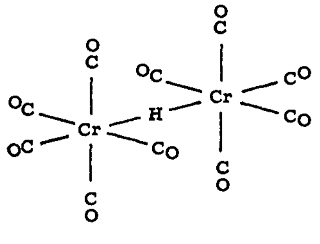


Figure 2. Hydride absorption in the nmr spectrum of $Na[W_2H(CO)_{10}]$ (THF solution).

Extended reaction times do not cause any marked change in these spectra, although some slight decomposition with precipitation of metal does occur slowly. The complex anions may be isolated as their tetraethylammonium salts and these stable air-sensitive derivatives have infrared spectra in the carbonyl region essentially the same as those observed for the reaction solutions (Table II). There is therefore little doubt that the initial reaction product and the isolated salt contain the same anion.

Analysis of the tetraethylammonium salts supports the formulation $[(C_2H_5)_4N][M_2H(CO)_{10}]$ (Table I), the hydride ligand being included at this stage to preserve electroneutrality. Several possible structures can be drawn for these anions, but the presence of only three carbonyl stretching vibrations strongly suggests a structure with a fourfold axis of symmetry (D_{4h}, **2**, or D_{4d}, **3**).[18] Less symmetrical structures (**4**, for example) would probably show a larger number of bands (four A_1, one B_1, and four B_2 infrared-active modes for a structure of C_{2v} symmetry). Structures involving bridging carbonyl groups can be eliminated owing to the lack of observed bands in the 1700–1800-cm^{-1} region. The most likely structures which fit the observed infrared spectrum are either the $Mn_2(CO)_{10}$-like structure which has staggered carbonyl groups and hence D_{4d} symmetry (**3**) or its eclipsed-carbonyl D_{4h} counterpart (**2**). Infrared spectra alone cannot distinguish between these structures, both of which have the novel feature of the hydride ligand being located directly between the two metal atoms.



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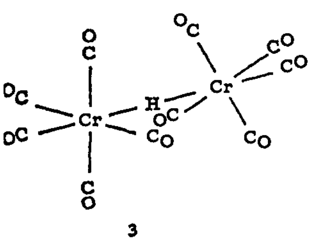

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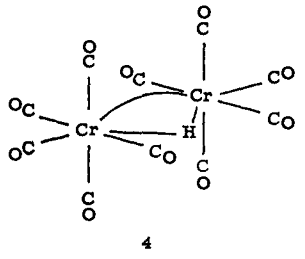

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The presence of a hydride ligand and the diamagnetism of these complexes was confirmed from the high-field proton nuclear magnetic resonance spectra of both the reaction solutions and the pure complexes (Table II). The chromium and molybdenum complexes showed a singlet resonance, as expected, while the tungsten complex showed a five-line pattern (Figure 2), and is thus of particular interest. The strong central line of this absorption is due to hydride ligands bonded to tungsten nuclei of zero spin. Immediately flanking this singlet is a weak doublet (J = 3.6 cps) which is attributed to coupling between the metal–hydrogen and ^{13}C (1.1% abundant) in the carbonyl groups (the intensity of this absorption leads to an estimate of 4 ± 1 carbonyl groups attached to tungsten). Finally, the outer doublet (J = 41.9 cps) is due to coupling between the hydride ligand and the ^{183}W isotope (14.28% abundant, $I = {}^1/_2$).

It is of considerable interest that a similar nmr spectrum has been previously observed for solutions of $[\pi\text{-}C_5H_5W(CO)_3]_2$ in sulfuric acid due to the protonated species $[(\pi\text{-}C_5H_5)_2W_2H(CO)_6]^+$,[19] although the coupling to ^{13}CO was apparently not seen. Attempts were made to correlate the relative intensities of the lines constituting the observed triplet absorption with a number of expected structures, and a structure involving intramolecular hydrogen exchange between two equivalent coordination sites (structure A in Table III) was considered the most likely.[19] In Table III are summarized the spectra calculated for various possible structures, both static (A, C, D) and dynamic (B).

It is evident from Table III that structure A is not consistent with the observed spectra and the introduction of coupling between hydrogen and the far tungsten nucleus does not improve the agreement. The quintets calculated for structures B–D must be compared with

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[18] F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, 84, 4432 (1962), and references therein.

[19] A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 3653 (1962).

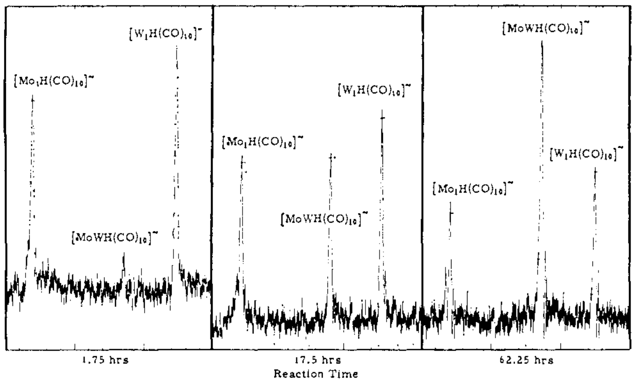
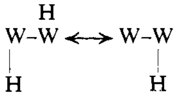
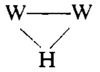


Figure 3. Reaction between $[(C_2H_5)_4N][Mo_2H(CO)_{10}]$ and $[(C_2H_5)_4N][W_2H(CO)_{10}]$ in THF at 80°, as followed by nmr.

the triplet observed for $[W_2H(CO)_{10}]^-$ (the observed coupling to ^{13}CO being neglected for this purpose). The difference between the observed spectrum and that calculated for B–D lies only in the absence of the weak outermost lines of the quintet. Unfortunately, it is only from the intensity of these outermost lines that the dynamic (B) and bridging structures (C, D) can be distinguished. Energetic but unsuccessful attempts to find these weak absorptions using concentrated solutions of the complex and an HR-100 spectrometer were made. The signal-to-noise ratio of the spectrum was such that absorptions of the expected intensity would have been easily visible. It is of interest that $[(C_5H_5)_2W_2H(CO)_6]^+$ also showed only a triplet hydride resonance, and we have confirmed this observation, although the quality of the spectrum was relatively poor and the outer lines of the quintet might not have been visible above the noise.

Table III. Observed and Calculated Proton Nmr Spectra for Possible Structures of $[W_2H(CO)_{10}]^-$ [a]

	Structure[b]	Calcd nmr spectrum
A	W–W	1:12:1 triplet
B		0.08:1:6:1:0.08 quintet (separation = $^1/_4 J_{H^{183}W}$)
C		0.04:1:6:1:0.04 quintet (separation = $^1/_2 J_{H^{183}W}$)
D	W–H–W	
		Observed nmr spectrum
	$[W_2H(CO)_{10}]^-$	1:6:1 triplet, τ 22.60, $J_{H^{183}W}$ = 41.9 cps
	$[(\pi\text{-}C_5H_5)_2W_2H(CO)_6]^{+c}$	1:6:1 triplet, τ 34.77, $J_{H^{183}W}$ = 38.6 cps

[a] This treatment follows that of Davison, *et al.*,[19] with the added simplification that long-range hydrogen–tungsten coupling is assumed to be zero. In addition, we have included structure D which represents the D_{4h} or D_{4d} structures (2 or 3, respectively), whereas Davison, *et al.*, represented their static bridged structure to be of lower symmetry (C, equivalent to 4). The calculated spectra for structures 3 and 4 are identical. [b] The five carbonyl groups attached to each tungsten have been omitted for clarity. [c] See ref 19.

Structures B, C, and D thus appear to be equally probable from the nmr evidence alone. However, in view of the infrared and X-ray evidence in favor of structure **2**, the lack of more satisfactory agreement with the calculated nmr spectrum is difficult to explain and may result from as yet unappreciated subtleties in the structure. More positive evidence in favor of **2** can be obtained from the nmr spectra of the heterobimetallic hydridocarbonyl anions.

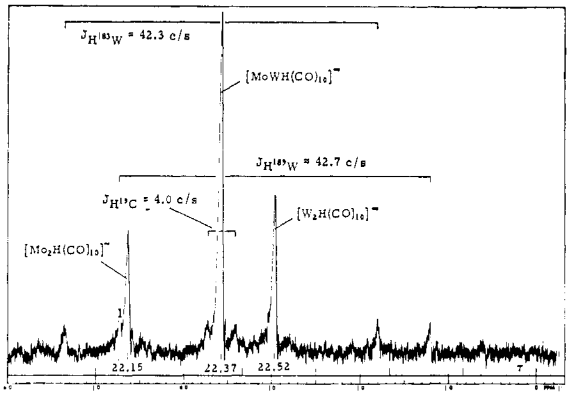


Figure 4. Hydride absorptions in the nmr spectrum of the equilibrium mixture of $[Mo_2H(CO)_{10}]^-$, $[MoWH(CO)_{10}]^-$, and $[W_2H(CO)_{10}]^-$ (THF solution).

The Heterobimetallic Anions, $[MM'H(CO)_{10}]^-$. Consideration of the bonding in the binuclear anions, $[M_2H(CO)_{10}]^-$, led to an investigation of the synthesis of complexes in which two different metal atoms may be connected by a hydrogen bridge. We find, for example, that on heating $[(C_2H_5)_4N][Mo_2H(CO)_{10}]$ and $[(C_2H_5)_4N][W_2H(CO)_{10}]$ together in tetrahydrofuran at 80°, a third hydride absorption in the high-field region of the nmr spectrum slowly grows between, and at the expense of, the absorptions already assigned to the two homobimetallic anions (Figure 3). After about 60 hr, the intensity of this intermediate absorption which is due to the mixed anion $[MoWH(CO)_{10}]^-$ reaches a maximum corresponding to a statistical distribution of hydride ligands between the three binuclear species. Although the reaction has been studied only with equimolar quantities of the homobimetallic anions, it seems likely that this is another example of a statistically determined scrambling reaction, with an equilibrium constant of four.[20]

$$[Mo_2H(CO)_{10}]^- + [W_2H(CO)_{10}]^- \rightleftharpoons 2[WMoH(CO)_{10}]^- \quad (2)$$

The same mixture of anionic complexes can be obtained by coreduction of equimolar amounts of molybdenum and tungsten hexacarbonyls with sodium borohydride in refluxing tetrahydrofuran. Complete reaction with attainment of equilibrium is reached in less than 16 hr under these conditions (Figure 4).

All three of the group VI metal heterobimetallic anions have been prepared by the coreduction method. Since no effort was made to separate the mixture of anions, the infrared spectra of the reaction solutions (Table II) contain bands due to all three species. The infrared spectra are, however, much simpler than expected, and only the reactions involving chromium carbonyl anions contained extra resolved absorptions which may be due to the mixed species. This may be due to an averaging process similar to that suggested

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(20) For other examples of scrambling reactions, see the work of Van Wazer and his co-workers, for example, D. W. Matula, L. C. D. Groenweghe, and J. R. Van Wazer, *J. Chem. Phys.*, 41, 3105 (1964), and references therein.

by Kaesz to account for the unexpectedly simple infrared spectrum of $[MnRe(CO)_{10}]$.[21]

The high-field resonance of the hydride ligand in the heterobimetallic anions always occurs between those due to the two constituent homobimetallic anions and closer to that of the heavier metal. It is probably not safe to conclude from this that the bridge bond in the heterobimetallic species is asymmetric with stronger bonding to the heavier metal, owing to the complex nature of the factors which determine chemical shifts in transition metal hydrides.[22a]

The 1:12:1 triplet absorption observed for $[MoWH(CO)_{10}]^-$ (Figure 4) is in exact agreement with the spectra calculated for each of the structures analogous to B–D in Table III. It is interesting to note that in $[(C_5H_5)_2MoWH(CO)_6]^+$ the proton resonance was also a 1:12:1 triplet and that it occurred midway between the absorptions due to the two corresponding homobimetallic species, although the position is probably only accidental.[19]

The values of $J_{H^{183}W}$ for the complexes $[W_2H(CO)_{10}]^-$, $[MoWH(CO)_{10}]^-$, $[CrWH(CO)_{10}]^-$, $[(C_5H_5)_2W_2H(CO)_4]^+$, and $[(C_5H_5)_2MoWH(CO)_4]^+$ all fall within the narrow range 38–43 cps and close to the value of 37.7 cps observed for $[C_5H_5WH(CO)_3]$.[22] In a rapidly exchanging structure such as B in Table III, the observed coupling constant is the average of the true coupling constants in the two possible environments and, in mixed complexes such as $[MoWH(CO)_{10}]^-$, this will be half the true $J_{H^{183}W}$. The very similar values of $J_{H^{183}W}$ in both the binuclear complexes and the related mononuclear complex noted above argues against an averaging process such as occurs in structure B (Table III). A similar argument may be made concerning the magnitude of the observed coupling constant in $[W_2H(CO)_{10}]^-$ but, in this case, there is some uncertainty owing to the unknown magnitude of the long-range hydrogen–^{183}W coupling.

The $[M_2(CO)_{10}]^{2-}$ Anions. The reduction of the group VI metal hexacarbonyls with sodium amalgam, using ultraviolet light to accelerate the reaction, has yielded a series of complex anions which have been isolated as their tetraethylammonium salts. Analytical and conductivity data are consistent with the formulation $[(C_2H_5)_4N]_2[M_2(CO)_{10}]$ although other polynuclear formulations cannot be excluded. The infrared spectra in the carbonyl region of the reaction solutions and of the isolated salts are very similar, although the solution spectra do show a number of additional weak bands due to minor unidentified products. An outstanding feature of these spectra is the presence of strong bands in the bridging carbonyl region. These complex anions are thus not identical with the $[M_2(CO)_{10}]^{2-}$ series previously prepared by Behrens[4,5] which are reported to have a manganese carbonyl-like structure from their infrared spectra.[23] It is possible that the two series of anions are isomeric and bear a similar structural relationship to each other as do the two isomeric forms of dicobalt octacarbonyl.[24]

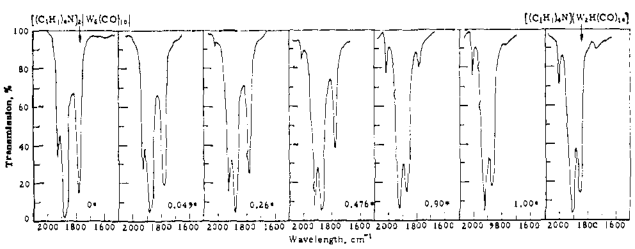

Figure 5. Infrared study of the reaction of $[(C_2H_5)_4N]_2[W_2(CO)_{10}]$ with HCl (DMSO solution). The asterisk denotes equivalents of HCl added.

The $[M_2H(CO)_{10}]^-$ and $[M_2(CO)_{10}]^{2-}$ series of anions are connected by an acid–base relationship and $[M_2(CO)_{10}]^{2-}$ reacts rapidly and quantitatively with acids to give $[M_2H(CO)_{10}]^-$ (Figure 5). The reverse reaction occurs only in the presence of excess strong base, owing to the weakly acidic nature of $[M_2H(CO)_{10}]^-$, to give a product with an infrared spectrum identical with the original dianion. Behrens has reported that his $[M_2(CO)_{10}]^{2-}$ series of complexes are hydrolyzed by water to give $[M_2H(CO)_{10}]^-$,[4,5] and we have observed similar reactions. Our attempts to further protonate $[M_2H(CO)_{10}]^-$ with anhydrous hydrogen chloride were unsuccessful, although this is now not surprising in view of the lack of coordination sites available for an additional proton in **2**.[17]

Attempts to prepare mercury derivatives of the $[M_2(CO)_{10}]^{2-}$ anions by reaction with mercuric chloride were unsuccessful in contrast to the ready formation of mercury derivatives of other carbonyl anions (for example, $[Mn(CO)_5]^-$, $[Fe(CO)_4]^{2-}$, $[C_5H_5Mo(CO)_3]^-$, under similar conditions.[25] Perfluoropropyl iodide, however, reacted with $[Cr_2(CO)_{10}]^{2-}$ to give the known anion $[CrI(CO)_5]^-$,[14] as expected.[25]

Discussion

Structure and Bonding in the $[M_2H(CO)_{10}]^-$ Anions. The spectroscopic evidence discussed above strongly suggests a symmetrical hydrogen-bridged structure for $[M_2H(CO)_{10}]^-$ and is entirely consistent with the D_{4h} structure, **2**, recently reported for $[Cr_2H(CO)_{10}]^-$.[17] The X-ray crystallographic examination was not able to locate the position of the unique hydrogen atom, but the symmetry of the anion and the lack of other suitably placed coordination sites strongly suggest that the hydride ligand lies on the fourfold axis connecting the two $Cr(CO)_5$ fragments. The observed chromium–chromium distance in $[Cr_2H(CO)_{10}]^-$ is 3.41 A which leads to an *average* Cr–H bond length of 1.7 A, very similar to the estimated Mo–H distance of 1.8 A in $[(C_5H_5)_2Mo_2H(P(CH_3)_2)(CO)_4]$[9] and to the average observed Mn–H distance of 1.65 A in $[Mn_3H(B_2H_6)(CO)_{10}]$.[12] However, it must be emphasized that this Cr–H distance is only an average, since there is no evidence presently available to distinguish between single and double minimum potential functions for the bridging hydrogen.[26] It is entirely possible that the hydride ligand may be oscillating between two equivalent sites on the chromium–chromium axis, and in this case the chromium–hydrogen bond distance would be

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[21] N. Flitcroft, D. K. Huggins, and H. D. Kaesz, *Inorg. Chem.*, 3, 1123 (1964).

[22] (a) M. L. H. Green and D. J. Jones, *Advan. Inorg. Chem. Radiochem.*, 7, 115 (1965); (b) A. Davison, J. A. McCleverty, and G. Wilkinson, *J. Chem. Soc.*, 1133 (1963).

[23] W. Hieber, W. Beck, and G. Braun, *Angew. Chem.*, 72, 795 (1960).

[24] G. Bor, *Spectrochim. Acta*, 19, 2065 (1963), and references therein.

[25] R. B. King, *Advan. Organometal. Chem.*, 2, 157 (1964).

[26] J. A. Ibers, *Ann. Rev. Phys. Chem.*, 16, 375 (1965).

less than 1.7 A. However, there appears to be little doubt that $[Cr_2H(CO)_{10}]^-$, and the analogous molybdenum and tungsten complex anions, represent further examples of hydride ligand bridging two transition metals.[9,12,13] This series, however, is particularly interesting in that it contains the only complexes so far known in which two transition metals are held together *solely* by a bridging hydride ligand. It is therefore of interest to briefly consider the mode of bonding in the $[M_2H(CO)_{10}]^-$ complexes.

If the structure **2** can be considered to obtain throughout the series, the $[M_2H(CO)_{10}]^-$ anions may be constructed from two $[M(CO)_5]^0$ square-pyramidal fragments so arranged that vacant octahedral-type metal orbitals point directly toward each other. The hydride anion may then be placed directly between them. The rest of the framework is made up of chromium–carbon monoxide bonds which have just the right number of electrons for a stable configuration, and can thus be neglected for the purpose of this simple treatment. The two metal orbitals and the single hydrogen 1s orbital may then be combined to give three molecular orbitals, bonding, nonbonding, and antibonding, respectively. Two electrons are available for these three orbitals and they will fill the lowest energy bonding orbital. From these considerations, it appears that the two halves of the molecule are held together by a linear three-center, two-electron bond. This type of bonding has been previously suggested for the (bent) transition metal hydrogen bridge bonds in $[Fe_3H(CO)_{11}]^-$ [13] and $[(C_5H_5)_2Mo_2H(P(CH_3)_2)(CO)_4]$,[9] and the linear version may also be proposed for $[(C_5H_5)_2M_2H(CO)_6]^+$. There also exists a formal similarity to the mode of bridge bonding in the boron hydrides[27] and in the hydrogen bond itself, although in the latter case, both the bonding and the nonbonding orbitals are filled.[28]

The structure and possible electron-deficient nature of the bridge bonds in the $[M_2H(CO)_{10}]^-$ anions led to a search for evidence of dissociation. The scrambling reactions observed between, for example, $[Mo_2H(CO)_{10}]^-$ and $[W_2H(CO)_{10}]^-$ to give, at equilibrium, a statistical mixture of the two homobimetallic anions and $[MoWH(CO)_{10}]^-$, strongly suggests that dissociation does indeed occur at the bridge bond and that random recombination of the resulting monometallic fragments follows. There is no direct evidence to support the nature of the intermediate species, although $[HM(CO)_5]^-$ [3,4] and $[W(CO)_5]^0$ [29] have both been previously reported and could be formed by dissociation of $[M_2H(CO)_{10}]^-$.

$$[M_2H(CO)_{10}]^- \rightleftharpoons [MH(CO)_5]^- + [M(CO)_5]^0 \qquad (3)$$

Since coreduction of, for example, $Mo(CO)_6$ and $W(CO)_6$ with sodium borohydride yields the identical statistical mixture of anions, it is tempting to propose that the formation of the bimetallic species occurs by a similar process, the monometallic intermediates being produced by reaction between the hexacarbonyl and borohydride anion (eq 4–7). It is interesting that equilibrium is reached more rapidly in the coreduction than in the scrambling reactions. This suggests

$$[BH_4]^- + M(CO)_6 \longrightarrow [HM(CO)_5]^- + {}^1/_2B_2H_6 + CO \qquad (4)$$

$$M(CO)_6 \xrightarrow{S(solvent)} [M(CO)_5]^0 \text{ (or } [SM(CO)_5]) \qquad (5)$$

$$[HM(CO)_5]^- + [M(CO)_5]^0 \rightleftharpoons [M_2H(CO)_{10}]^- \qquad (6)$$

or

$$[HM(CO)_5]^- + M(CO)_6 \rightleftharpoons [M_2H(CO)_{10}]^- + CO \qquad (7)$$

that the monometallic species are produced more rapidly in the coreduction reactions, as might be expected.

The Infrared Spectra of the $[M_2H(CO)_{10}]^-$ Anions. In view of the recent work of Cotton and Wing,[30] it is of interest to compare the infrared spectra of $[M_2H(CO)_{10}]^-$ with those of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$. Qualitatively, the spectra are very similar, each showing the three bands now known to be typical of symmetrical monosubstituted octahedral pentacarbonyl complexes. Like $Mn_2(CO)_{10}$, the $[M_2H(CO)_{10}]^-$ anions show much greater intensity in the highest frequency band than do the related mononuclear pentacarbonyl complexes, $[MnX(CO)_5]$ (X = H, halogen).[31] This effect has been attributed in the $Mn_2(CO)_{10}$ case to coupling between the equatorial carbonyl vibrations *via* the metal–metal bond.[30] It may be argued that an analogous coupling is to be expected in $[M_2H(CO)_{10}]^-$, but that any attenuation which might be caused by the bridging hydride ligand does not greatly affect the observed intensity. It has also been proposed that the energy difference between this highest frequency band and the band of next highest energy, the intense absorption of E symmetry, is also affected by coupling between the two halves of the molecule.[30] This difference is found to be about 100 cm^{-1} in the mononuclear complexes and is reduced to about 50 cm^{-1} in $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$. The corresponding band separations in $[M_2H(CO)_{10}]^-$ are in the range 100–110 cm^{-1} and, hence, are presumably more sensitive to the attenuating effect of the hydride ligand than are the band intensities.

A more quantitative treatment of the effect of the bridging hydride ligand on the infrared spectrum must await a complete assignment of the carbonyl vibrational spectra, and this is at present hampered by our inability to determine Raman spectra of the yellow solutions of $[M_2H(CO)_{10}]^-$.

Hydride Relaxation Times. It has been reported that the relaxation times (T_1) of the hydride ligand in $[Mo_2H(CO)_{10}]^-$ and $[W_2H(CO)_{10}]^-$ are long (*ca.* 2 min) and that this may be diagnostic of hydrogen bridge bonding.[15] We have essentially confirmed these observations and also find that T_1 of $[Cr_2H(CO)_{10}]^-$ is short and not easily measured.[32] In view of this difference and the lack of similar data for a range of transition metal hydrides, both bridged and terminal, we conclude that relaxation times are not yet a useful diagnostic measurement.

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