

**Table V.** Some H-F Coupling Constants of Vinylic Protons and CF<sub>3</sub> Groups

Compound	$J_{12}$	$J_{13}$	$J_{23}$	Ref
$[(C_2H_5)_3P]_2PtClC(CF_3)=C(CF_3)H$	9.6	...	0	This work
$(CO)_5Re(CF_3)C=C(CF_3)H-trans$	9.1	2.5	..	29
$(CO)_5Mn(CF_3)C=C(CF_3)H-trans$	9.6	2.3	..	29
$(CH_3)_2As(CF_3)C=C(CF_3)H-trans$	8.3	2.0	..	15
$(CH_3)_2As(CF_3)C=C(CF_3)H-cis$	8.3	...	0	15
$CH_3(C_6H_5)_2As(CF_3)C=C(CF_3)H-cis$	8.5	...	0	15
$CH_3(C_6H_5)_2As(CF_3)C=C(CF_3)H-trans$	8.5	2	..	15

for *trans* isomers of related derivatives<sup>29</sup> the coupling constant is of the order of 1.5–2.5 cps and is zero for *cis* isomers (Table V). The multiplet at –20.7 ppm must be due to the CF<sub>3</sub> group geminal to the vinylic proton and consists of 18 peaks which are formed by

(29) J. B. Wilford and F. G. A. Stone, *Inorg. Chem.*, **4**, 93 (1965).

coupling with the latter proton, fluorine atoms in the other CF<sub>3</sub> group, and to <sup>195</sup>Pt. The value of  $J_{CF_3-CF_3} = 12.2$  cps is in excellent agreement with those reported for other *cis* isomers,<sup>15</sup> whereas analogous *trans* isomers<sup>15,29</sup> give  $J_{CF_3-CF_3}$  of the order of 1–3 cps. This high value of  $J_{CF_3-CF_3}$  in the *cis* configuration has been attributed to through-space coupling.<sup>29</sup> The evidence therefore strongly favors the *cis*-olefinic confirmation for our Pt(II) compound, and, as final configuration, the excellent agreement of the  $J_{Pt-C-C-CF_3}$  values for this compound and the *trans*-perfluoropropenyl derivative (both 5.82 cps) may be cited. It is interesting that there is no spectroscopic evidence for a *trans* isomer produced from this reaction of perfluorobut-2-yne.

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## Organometallic Compounds with Metal–Metal Bonds. VI. Preparation and Infrared Spectra of the Carbonylmetalate Ions [[OC]<sub>5</sub>M–M'(CO)<sub>5</sub>]<sup>–</sup> (M = Mn, Re; M' = Cr, Mo, W)<sup>1</sup>

Udo Anders and W. A. G. Graham<sup>2</sup>

Contribution from the Department of Chemistry, University of Alberta,  
Edmonton, Alberta, Canada. Received July 21, 1966

**Abstract:** Reaction of NaM(CO)<sub>5</sub> with M'(CO)<sub>6</sub> affords the six new anions [[OC]<sub>5</sub>M–M'(CO)<sub>5</sub>]<sup>–</sup> (M = Mn, Re; M' = Cr, Mo, W), which were isolated as the yellow or orange tetraethylammonium salts. They are isoelectronic and isostructural with Mn<sub>2</sub>(CO)<sub>10</sub>. Their infrared spectra exhibit six terminal and no bridging carbonyl stretching frequencies, as expected for a C<sub>4v</sub> structure. Attempts to isolate a neutral protonated derivative were not successful.

Manganese carbonyl, Mn<sub>2</sub>(CO)<sub>10</sub>, and the anion [Cr<sub>2</sub>(CO)<sub>10</sub>]<sup>2–</sup> constitute an isoelectronic pair. The manganese derivative is among the most fully characterized of all carbonyl compounds, both by infrared spectroscopy<sup>3,4</sup> and by X-ray diffraction.<sup>5</sup> By contrast, the structure of the chromium species must be regarded as unsettled. The salt Na<sub>2</sub>[Cr<sub>2</sub>(CO)<sub>10</sub>] was first obtained by Behrens and Haag,<sup>6</sup> from reaction of chromium hexacarbonyl with sodium borohydride in liquid ammonia at 60°. The first infrared results<sup>7</sup> favored a structure without bridging carbonyl groups, similar to that of manganese carbonyl. Very recently, it has been found by Hayter<sup>8</sup> that an ion of composition [Cr<sub>2</sub>(CO)<sub>10</sub>]<sup>2–</sup> is formed in the reduction of a tetrahydrofuran solution of chromium hexacarbonyl by

(1) Part V: D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, **5**, 2222 (1966).

(2) To whom correspondence should be addressed.

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

(4) F. A. Cotton and R. M. Wing, *ibid.*, **4**, 1328 (1965).

(5) L. F. Dahl, E. Ishishi, and R. E. Rundle, *J. Chem. Phys.*, **26**, 1750 (1957); L. F. Dahl and R. E. Rundle, *Acta Cryst.*, **16**, 419 (1963).

(6) H. Behrens and W. Haag, *Chem. Ber.*, **94**, 312 (1961); the molybdenum analog was also reported by these workers, and the tungsten analog by H. Behrens and J. Vogl, *ibid.*, **96**, 2220 (1963).

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

(8) R. G. Hayter, *J. Am. Chem. Soc.*, **88**, 4376 (1966). We thank Dr. Hayter for making his manuscript available in advance of publication.

sodium amalgam; however, bridging carbonyl groups are indicated by the infrared spectrum of Hayter's compound.

Additional interest in the nature of the [Cr<sub>2</sub>(CO)<sub>10</sub>]<sup>2–</sup> species arises from recent studies<sup>8–10</sup> of its protonated derivative [HCr<sub>2</sub>(CO)<sub>10</sub>]<sup>–</sup>. The latter ion contains a linear, and probably symmetrical Cr–H–Cr unit, which has been described as a protonated metal–metal bond,<sup>9</sup> or, more generally, as a three-center–two-electron bond.<sup>10</sup>

Consideration of the isoelectronic pair M<sub>2</sub>(CO)<sub>10</sub>–[M'<sub>2</sub>(CO)<sub>10</sub>]<sup>2–</sup> (M = Mn, Re; M' = Cr, Mo, W)<sup>11</sup> led us to believe that a third, intermediate member of the series should exist, namely [(CO)<sub>5</sub>M–M'(CO)<sub>5</sub>]<sup>–</sup>. We describe in this paper the preparation and infrared spectra of these new anions.

### Experimental Section

Reactions were carried out and products purified under a nitrogen atmosphere. Diglyme and THF<sup>12</sup> were freshly distilled from lith-

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

(10) L. B. Handy, P. M. Treichel, L. F. Dahl, and R. G. Hayter, *J. Am. Chem. Soc.*, **88**, 366 (1966).

(11) This symbolism is used throughout.

(12) Diglyme = diethylene glycol dimethyl ether; THF = tetrahydrofuran.

Table I. Analytical Data

Compound	Color	—Carbon, %—		—Hydrogen, %—		—Nitrogen, %—		—Oxygen, %—	
		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> N[MnCr(CO) <sub>10</sub> ] <sup>a</sup>	Yellow	41.79	41.73	3.90	4.06	2.71	2.44	30.93	28.66
(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> N[MnMo(CO) <sub>10</sub> ]	Yellow	38.52	39.15	3.59	3.66	2.50	2.57	28.51	26.57
(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> N[MnW(CO) <sub>10</sub> ]	Yellow	33.31	34.40	3.10	3.29	2.16	2.25	24.65	23.32
(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> N[ReCr(CO) <sub>10</sub> ]	Orange	33.33	32.79	3.11	3.10	2.16	1.74	24.67	24.46
(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> N[ReMo(CO) <sub>10</sub> ]	Orange-yellow	31.22	31.02	2.91	2.95	2.02	2.05	23.10	23.30
(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> N[ReW(CO) <sub>10</sub> ] <sup>b</sup>	Orange-yellow	27.70	27.68	2.58	2.65	1.80	1.75	20.50	20.89

<sup>a</sup> Manganese: calcd, 10.62; found, 9.85. Chromium: calcd, 10.05; found, 9.34. <sup>b</sup> Rhenium: calcd, 23.86; found, 23.63. Tungsten: calcd, 23.56; found, 22.88.

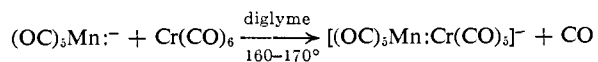
um aluminum hydride. The microanalyses of Table I were carried out by Alfred Bernhardt Mikroanalytisches Laboratorium, Mülheim, and by Pascher Mikroanalytisches Laboratorium, Bonn. Infrared spectra (Table II, Figure 1) were determined on fresh THF solutions using a Perkin-Elmer Model 337 (grating) infrared spectrometer, with expansion on an external recorder and CO-DBr calibration as previously described.<sup>13</sup> The following detailed procedure for [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N]<sup>+</sup>[(OC)<sub>5</sub>MnCr(CO)<sub>5</sub>]<sup>-</sup> can be applied with only minor variations to other members of the series.

**Preparation of [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N]<sup>+</sup>[(OC)<sub>5</sub>Mn-Cr(CO)<sub>5</sub>]<sup>-</sup>.** Manganese carbonyl (3.0 g, 7 mmoles) in 60 ml of diglyme was magnetically stirred at room temperature over sodium amalgam (0.7 g of sodium with 8 ml of mercury) for 90 min. The diglyme solution of NaMn(CO)<sub>5</sub> was decanted into another flask and to it was added chromium hexacarbonyl (3.0 g, 13.5 mmoles). The solution was stirred magnetically in an oil bath at 160–175°; evolution of carbon monoxide ceased after 2 hr, indicating completion of the reaction. Addition of *n*-pentane to the cold diglyme solution produced a red oil, from which supernatant diglyme was withdrawn with a syringe. The oil was washed twice with more *n*-pentane, in which it was completely insoluble. Finally, residual *n*-pentane was removed at reduced pressure. The oil was then shaken vigorously with a solution of 3 g of (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NCl in 40 ml of water. The yellow precipitate was filtered off on a sintered glass funnel and washed successively with two 20-ml portions of water, 20 ml of ethanol, and three 20-ml portions of ether. The product was then dried under high vacuum (yield 5.0 g, 71%). An analytical sample was prepared by recrystallization from 95% ethanol in a Schlenk tube.

## Results and Discussion

Six new anions of the general formula [(CO)<sub>5</sub>M-M'(CO)<sub>5</sub>]<sup>-</sup> have been prepared and characterized by elemental analysis (Table I). They are conveniently isolated as their beautifully crystalline, yellow to orange tetraethylammonium salts. These survive brief handling in air, are stable for months at room temperature under nitrogen, and darken when heated to temperatures near 180°. Qualitatively, stability increases from the Mn-Cr to the Re-W derivative.

The reaction by which these derivatives are prepared is of rather general interest.



To emphasize the essential feature of this reaction, we have placed a symbolical lone pair of electrons on the pentacarbonylmanganese anion. We feel that the electron pair has heuristic value insofar as reactions are concerned, but we do not imply any stereochemical significance for the lone pair.<sup>14</sup> The “donor” character of (OC)<sub>5</sub>Mn:⁻ is thus clearly shown in the formation of the adduct [(OC)<sub>5</sub>Mn:BH<sub>3</sub>]<sup>-</sup>.<sup>15</sup> Although the

(13) W. Jetz, P. B. Simons, J. A. J. Thompson, and W. A. G. Graham, *Inorg. Chem.*, **5**, 2217 (1966).

(14) We thank a referee for emphasizing this distinction. Infrared and Raman studies on Co(CO)<sub>4</sub><sup>2-</sup> and Fe(CO)<sub>4</sub><sup>2-</sup> indicate tetrahedral structures, and it may be concluded that electron pairs do not occupy coordination positions in these anions. We assume provisionally that Mn(CO)<sub>5</sub><sup>-</sup> has the D<sub>3h</sub> rather than the C<sub>4v</sub> structure.

(15) G. W. Parshall, *J. Am. Chem. Soc.*, **86**, 361 (1964).

nucleophilicity of metal carbonyl anions is well established in halide displacement reactions,<sup>16</sup> the deliberate use of these anions as ligands to displace carbon monoxide has heretofore not been reported. We suggest that reactions of this general type may constitute an important process in the “base reactions” of metal carbonyls, wherein complex polynuclear species are formed. Indeed, the “base reaction” of (OC)<sub>5</sub>Mn:⁻ with Fe(CO)<sub>5</sub> has recently been found<sup>17</sup> to produce the new mixed metal anion [MnFe<sub>2</sub>(CO)<sub>12</sub>]<sup>-</sup>.

Other processes in the literature are clarified by a full appreciation of the ability of carbonyl anions to displace carbon monoxide. For example, the facile formation of (OC)<sub>5</sub>Re-Co(CO)<sub>4</sub> by loss of carbon monoxide from the salt [(OC)<sub>6</sub>Re]<sup>+</sup>[Co(CO)<sub>4</sub>]<sup>-</sup><sup>18</sup> is undoubtedly a manifestation of this phenomenon in which Co(CO)<sub>4</sub><sup>-</sup> as nucleophile displaces carbon monoxide from the cation.

**Infrared Spectra.** The carbonyl stretching frequencies of the new compounds, recorded in tetrahydrofuran solution to achieve sufficient solubility, are given in Table II. There are no bridging carbonyl

Table II. Carbonyl Stretching Frequencies<sup>a</sup>

Ion	ν(CO), cm <sup>-1</sup>
[MnCr(CO) <sub>10</sub> ] <sup>-</sup>	2063 w, 1990 s, 1950 ss, 1925 m, 1896 s, 1865 m
[MnMo(CO) <sub>10</sub> ] <sup>-</sup>	2067 w, 2007 s, 1946 ss, 1920 m, 1904 w, 1866 s
[MnW(CO) <sub>10</sub> ] <sup>-</sup>	2066 w, 2007 s, 1948 ss, 1926 m, 1898 s, 1861 m
[ReCr(CO) <sub>10</sub> ] <sup>-b</sup>	2078 w, 1985 s, 1961 ss, 1928 m, 1888 s, 1858 m
[ReMo(CO) <sub>10</sub> ] <sup>-</sup>	2073 w, 2009 s, 1954 ss, 1925 m, 1901 s, 1853 m
[ReW(CO) <sub>10</sub> ] <sup>-</sup>	2076 w, 2009 s, 1958 ss, 1930 m, 1893 s, 1857 m

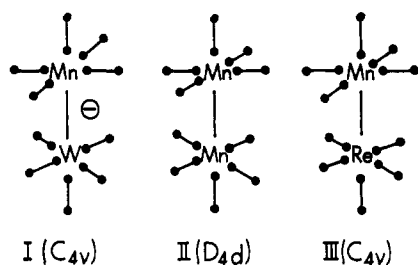
<sup>a</sup> Tetraethylammonium salts in tetrahydrofuran freshly distilled from lithium aluminum hydride. <sup>b</sup> An additional weak band is observed at 2011 cm<sup>-1</sup>.

bands. The spectrum shows a definite tendency to change as the solutions age, and spurious peaks are observed unless the solvent is freshly purified. A typical spectrum is shown in Figure 1, which shows six well-resolved terminal bands. This is exactly the number predicted by group theory for a manganese carbonyl like arrangement of C<sub>4v</sub> symmetry, as in I. One can therefore assume that the new anions are isostructural as well as isoelectronic with manganese carbonyl (II).

(16) For a general review of the chemistry of metal carbonyl anions, cf. R. B. King, *Advan. Organometal. Chem.*, **2**, 157 (1964). For a number of specific displacement reactions with organometallic halides, cf. previous papers of this series.

(17) U. Anders and W. A. G. Graham, *Chem. Commun.*, 291 (1966).

(18) T. Kruck and M. Höfler, *Angew. Chem.*, **76**, 786 (1964); *Angew. Chem. Intern. Ed. Engl.*, **3**, 701 (1964); see also T. Kruck, M. Höfler, and M. Noack, *Chem. Ber.*, **99**, 1153 (1966).



It is of interest to compare the infrared spectra of the ions reported here with that of the neutral mixed compound III, for which six carbonyl bands are also predicted. Flitcroft, Huggins, and Kaesz<sup>3</sup> have made a detailed study of the infrared spectra of compounds II and III. For the symmetrical derivative II, three carbonyl stretching frequencies were predicted and three strong bands observed. For the mixed neutral species III, however, *only three (or possibly four) of the predicted six fundamentals were observed*, even with the optimum resolution possible in cyclohexane solution. In effect, the departure of the Re-Mn derivative III from  $D_{4d}$  symmetry was insufficient for the new modes to gain measurable intensity. In the species reported here, the metal atoms are more highly differentiated, and all possible bands are clearly seen. It is nonetheless surprising that such a gross difference in spectra should occur. One cannot dismiss the possibility that ion pairing, of the type recently discussed by Edgell, Yang, and Koizumi,<sup>19</sup> may be a contributing factor in the reduction of symmetry which occurs.

A possible interpretation of the spectrum is that it is a superposition of two sets of three bands, each set arising from one half of the ion.<sup>20</sup> Thus the first, third, and fourth bands of Figure 1 (at 2076, 1958, and 1930  $\text{cm}^{-1}$ ) resemble in their separation and intensity pattern the  $A_1^{(2)}$ , E, and  $A_1^{(1)}$  modes of  $\text{RMn}(\text{CO})_5$  derivatives.<sup>13,21</sup> The remaining bands (at 2009, 1893, and 1857  $\text{cm}^{-1}$ ) resemble strongly in position and pattern those of anions such as  $[\text{W}(\text{CO})_5\text{I}]^-$ .<sup>22</sup> We have used the Cotton-Kraihanzel treatment<sup>23</sup> to obtain approximate stretching force constants for each half of the ion with the assignments just discussed. The values for all six ions, with the ranges encountered, are as follows (all values in millidynes/angstrom): For the  $(\text{OC})_5\text{Mn}$  or  $(\text{OC})_5\text{Re}$  part,  $k_1 = 15.1 \pm 0.1$ ,  $k_2 = 16.0 \pm 0.1$ ,  $k_i = 0.29 \pm 0.01$ ; for the  $\text{Cr}(\text{CO})_5$ ,  $\text{Mo}(\text{CO})_5$ , and  $\text{W}(\text{CO})_5$  moieties, the values are  $k_1 = 14.1 \pm 0.1$ ,  $k_2 = 15.0 \pm 0.1$ ,  $k_i = 0.25 \pm 0.03$ . These values are reasonable, and in particular satisfy the requirement that  $k_1 < k_2$ .<sup>23</sup> If this interpretation is correct, there is negligible coupling of vibrations across the metal-metal bond. One might therefore infer that there is very little delocalization of charge across the metal-metal bond and that the primary structural representation may be  $(\text{OC})_5\text{Re}-\text{W}(\text{CO})_5^-$ . Such a localization of charge on one-half of the ion would account for the marked differentiation of the two  $\text{M}(\text{CO})_5$  groups.

**Attempted Protonation.** Anions of the type  $[\text{M}_2(\text{CO})_{10}]^{2-}$  readily acquire a proton<sup>6,8</sup> to form a rather

(19) W. F. Edgell, M. T. Yang, and N. Koizumi, *J. Am. Chem. Soc.*, **87**, 2563 (1965).

(20) We thank a referee for this suggestion.

(21) F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964); J. B. Wilford and F. G. A. Stone, *ibid.*, **4**, 389 (1965).

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

(23) F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962), whose notation we also use.

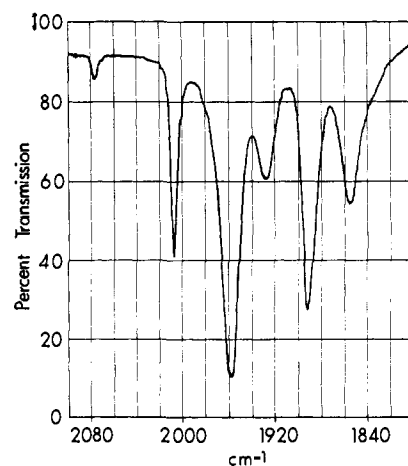


Figure 1. Carbonyl stretching region of the infrared spectrum of  $[(\text{C}_2\text{H}_5)_4\text{N}][(\text{OC})_5\text{Re}-\text{W}(\text{CO})_5]$ : about 1 mg/ml of tetrahydrofuran, 0.5-mm cells.

stable, well-characterized  $[(\text{OC})_5\text{M}-\text{H}-\text{M}(\text{CO})_5]^-$  derivative. On the other hand, a protonated derivative of  $\text{Mn}_2(\text{CO})_{10}$  has not been isolated, although a shift in position and extinction coefficient of the ultraviolet-visible absorption maximum in 98% sulfuric acid was considered to suggest that protonation did occur.<sup>24</sup> It was accordingly of interest to determine whether the anions  $[(\text{OC})_5\text{M}-\text{M}'(\text{CO})_5]^-$  could be protonated.

Reaction of yellow  $[(\text{C}_2\text{H}_5)_4\text{N}][(\text{OC})_5\text{MnCr}(\text{CO})_5]$  with 90% orthophosphoric acid under nitrogen gave a red material, insoluble in  $\text{H}_3\text{PO}_4$  and extractable in dichloromethane. All attempts at purification failed to give a definite product, although qualitative tests showed both chromium and manganese in the extract; removal of solvent and sublimation under high vacuum yielded only  $\text{Mn}_2(\text{CO})_{10}$ . The extract was scanned to  $\tau$  45 by nmr, revealing only a weak absorption at  $\tau$  18.0, rather close to the value  $\tau$  17.5 reported for  $\text{HMn}(\text{CO})_5$ .<sup>25</sup> Moreover, a similar solution prepared from  $[(\text{OC})_5\text{Mn}-\text{W}(\text{CO})_{10}]^-$  showed weak absorption at  $\tau$  18.2 but proton-tungsten spin-spin coupling was not observed. Mass spectrometry (MS-9) likewise provided no conclusive evidence for the existence of a neutral, and presumably volatile,  $\text{HMnCr}(\text{CO})_{10}$  species.

We conclude that the protonated derivative, if formed, is of low stability. This may be a consequence of the dissimilarity of the two metals. Although heterobinuclear species such as  $[(\text{OC})_5\text{Cr}-\text{H}-\text{Mo}(\text{CO})_5]^-$  have been identified in solution,<sup>8</sup> the three-center bond is in this case more nearly symmetrical than in the hypothetical  $(\text{OC})_5\text{Cr}-\text{H}-\text{Mn}(\text{CO})_5$ ; this is suggested by the infrared spectra of I and III, where the effective symmetry depends on whether the two metals are from the same or different periodic groups. On the other hand, a dissociation of  $[(\text{OC})_5\text{M}-\text{H}-\text{M}(\text{CO})_5]^-$  into  $[(\text{OC})_5\text{MH}]^-$  and  $[\text{M}(\text{CO})_5]$  has been suggested,<sup>8</sup> and it may be that the compound sought here is unstable with respect to a similar dissociation.

**Acknowledgment.** We acknowledge helpful discussions with Professor H. D. Kaesz, in whose laboratory a detailed analysis of the infrared spectra of these compounds, together with those of the neutral  $(\text{OC})_5\text{Re}-\text{Mn}(\text{CO})_5$  species, is in progress. We thank the National Research Council of Canada for financial assistance.

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

(25) F. A. Cotton, J. L. Down, and G. Wilkinson, *ibid.*, 833 (1959).