On a Rhodium Complex with Carbon Dioxide

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Abstract: By a reaction of $Rh_4(CO)_{12}$ with $P(C_6H_5)_3$, a rhodium carbonyl–triphenylphosphine complex (complex I) was prepared. This rhodium(0) complex is easily oxidized by molecular oxygen in aromatic solvents to give a new type of complex (II). Elemental analysis and other evidence indicate that this complex (II) has the molecular formula $Rh_2(CO)_2(CO_2)(P(C_6H_5)_3)_3L_n$ (L = benzene, toluene, *o*-, *m*-, and *p*-xylene, or mesitylene). By the use of $^{18}O_2$, the course of the oxidation reaction was examined. The infrared spectrum of the complex II was observed, and it was concluded that the coordinated carbon dioxide has a bent form.

In this paper we report of a new type of complex in which carbon dioxide is involved. It has been found by Wilkinson and his collaborators[1,2] that carbon dioxide does not react with tris(triphenylphosphine)platinum(0) at 25° in the complete absence of oxygen. On admission of oxygen, on the other hand, a reaction takes place and a carbonate complex, $(Ph_3P)_2PtCO_3$, is obtained. Our result is somewhat similar to theirs. On admission of oxygen into contact with a rhodium carbonyl–triphenylphosphine complex a new type complex was formed. Elemental analysis, infrared absorption measurements, and other examination of this complex indicated, however, that it has a bent carbon dioxide molecule (instead of the carbonate ion) in it. This paper describes this finding and discusses the mechanism of the reaction through which such a complex is formed.

Preparation and Analysis of Rhodium Complexes with Carbon Dioxide

By treating $Rh_4(CO)_{12}$ with $P(C_6H_5)_3$ in an inert gas atmosphere, a golden yellow material (complex I) is obtained. The analysis of this complex corresponds to $Rh_2(CO)_4(P(C_6H_5)_3)_4$. It shows absorption bands at 1763 and 1739 cm^{-1}, and this fact is considered to indicate that this complex has bridging carbonyls.

When complex I is exposed to a small amount of oxygen in a benzene solution, fine yellow needles (complex II) separate.

The crystal of complex II has a moderate stability in the air and is soluble in aromatic solvents, in CH_2Cl_2, and in $CHCl_3$. Complex II decomposes at 118° in the presence of oxygen, but in an inert atmosphere it does not melt even at 150°. An examination of the infrared spectra of complex II (Figure 1) and its deuterated derivatives obtained with $P(C_6D_5)_3$ and/or C_6D_6 shows that the complex II contains two different types of carbonyl groups at least, some $P(C_6H_5)_3$ groups, and another unknown ligand.

Thus, the strong absorption bands at 1970 and 1960 cm^{-1} are assignable to two different carbonyl groups. Twenty of the absorption bands in the 600–1900-cm^{-1} region (see Table I) are shifted when $P(C_6H_5)_3$ is changed to $P(C_6D_5)_3$. Therefore, these bands are attributed to the triphenylphosphine group. The weaker absorption bands at 1812, 1032, 683, 679, and 667 cm^{-1} are shifted on exchange of C_6H_6 to C_6D_6 and therefore are ascribed to the solvent molecule involved in the complex. Only three strong absorption bands, namely those at 1498, 1368, and 813 cm^{-1}, remain unchanged on $P(C_6H_5)_3 \rightarrow P(C_6D_5)_3$ and $C_6H_6 \rightarrow C_6D_6$ substitutions. In addition, only these three absorption bands show marked isotope shifts when $^{18}O_2$ (96.9 atom %) instead of ordinary $^{16}O_2$ is introduced into the reaction with complex I (Figure 2).

Table I. Infrared Spectra of Complex II[a]

ν, cm^{-1}		
$P(C_6H_5)_3$	$P(C_6D_5)_3$	Assignment
1812 (w)	1812 (w)	Benzene
1586 (w)	1549 (w)	Triphenylphosphine
1573 (w)	1535 (w)	Triphenylphosphine
1498 (s)	1498 (s)	Carbon dioxide
1479 (m)	1470 (w)	Triphenylphosphine
1438 (s)	1311 (m)	Triphenylphosphine
1434 (sh)		Triphenylphosphine
1368 (s)	1370 (s)	Carbon dioxide
1326 (w)	1278 (w)	Triphenylphosphine
1308 (w)	1272 (w)	Triphenylphosphine
1184 (w)		Triphenylphosphine
1159 (w)	1047 (m)	Triphenylphosphine
1117 (w)		Triphenylphosphine
1097 (m)		Triphenylphosphine
1093 (sh)	1029 (w)	Triphenylphosphine
1069 (w)		Triphenylphosphine
1032 (sh)	1032 (w)	Benzene
1026 (w)	953 (w)	Triphenylphosphine
996 (w)	871 (m)	Triphenylphosphine
813 (m)	816 (m)	Carbon dioxide
753 (s)	709 (w)	Triphenylphosphine
744 (s)	659 (w)	Triphenylphosphine
707 (s)	656 (w)	Triphenylphosphine
693 (s)	639 (w)	Triphenylphosphine
683 (m)	683 (m)	Benzene
679 (w)	677 (sh)	Benzene
667 (sh)	667 (sh)	Benzene
617 (w)	605 (w)	Triphenylphosphine

[a] s = strong, m = medium, w = weak, sh = shoulder.

On the basis of the infrared analysis it has been shown that complex II involves an oxygen-containing ligand which gives only three strong absorption bands (at 1498, 1368, and 813 cm^{-1}). One might consider that complex II is a carbonate complex. In fact, Wilkinson and his coworkers reported a platinum carbonate complex which gives vibrations at 1680, 1180, 980, 875, and 760 cm^{-1}.[1] Nakamoto,[3] on the other hand, showed that a unidentate cobalt(III) carbonate complex $(Co(NH_3)_5CO_3)NO_3 \cdot$

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[1] C. J. Nyman, C. E. Wymore, and G. Wilkinson, *Chem. Commun.*, 407 (1967).

[2] C. J. Nyman, C. E. Wymore, and G. Wilkinson, *J. Chem. Soc., A*, 561 (1968).

[3] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley & Sons, Inc., New York, N. Y., 1963, p 162.

Table II. Number (n) of Solvent Molecules (L) Incorporated into Complex II, $Rh_2(CO)_2[CO_2][P(C_6H_5)_3]_3L_n$

L	n	Calcd, % C	H	P	Rh	Found, % C	H	P	Rh
Benzene	1	64.62	4.40	7.94	17.58	64.45	4.88	7.23	17.21
Toluene	1	64.87	4.52	7.84	17.37	64.64	4.85		17.00
o-Xylene	0.5	63.94	4.41	8.11	17.96	63.44	4.37		
m-Xylene	0.5	63.94	4.41	8.11	17.96	63.80	4.83		16.40
p-Xylene	2	67.07	5.18	7.11	15.75	66.90	5.06		16.99
Mesitylene	0.75	64.73	4.61	7.85	17.40	64.98	4.90		17.40

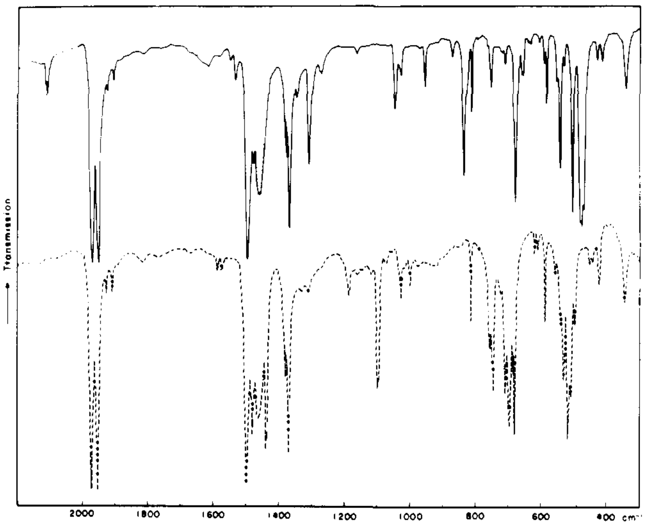

Figure 1. Infrared absorption spectra of complex II, $Rh_2(CO)_2(CO_2)(P(C_6H_5)_3)_3C_6H_6$ (broken line), and its deuterated derivative obtained with $P(C_6D_5)_3$, $Rh_2(CO)_2(CO_2)(P(C_6D_5)_3)_3C_6H_6$ (solid line); observed in Nujol mull.

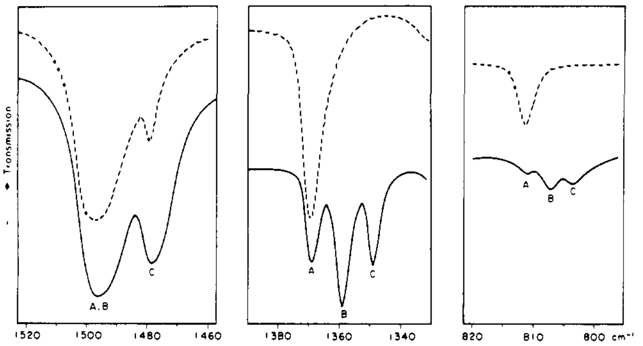

Figure 2. Effects of ^{18}O substitution on the infrared spectrum of complex II. Broken line: ordinary product; solid line: ^{18}O-containing complex II.

$0.5H_2O$ shows absorptions at 1482, 1365, 1052, 738, 690, and 351 cm^{-1}. Complex II does show absorption bands in these regions. However, their relative intensities are not similar to those of the carbonate complexes and, as has already been shown, most of them are to be assigned to the triphenylphosphine group or the solvent molecule (except the three bands mentioned above). Therefore, the ligand of complex II, now in question, is considered to be carbon dioxide rather than carbonate.

There is another evidence which supports the idea that the oxygen-containing ligand is CO_2 rather than CO_3. As is seen in Figure 2, the number of isotopic species distinguished by the infrared absorption measurement is only three. These three are assignable to $C^{16}O_2$, $C^{16}O$-^{18}O, and $C^{18}O_2$. If the ligand were carbonate, there should be at least four isotopic species distinguishable: $C^{16}O_3$, $C^{16}O_2{}^{18}O$, $C^{16}O^{18}O_2$, and $C^{18}O_3$.

The pyrolyzed gas of complex II has been examined by means of infrared absorption measurements and gas chromatographic analyses, which show that it includes carbon dioxide. The amount of the carbon dioxide was determined by trapping it on KOH. The molecular weight of complex II was found to be 1057 (vapor pressure osmometer in benzene solution). On the basis of these data, complex II is now considered to be $Rh_2(CO)_2(CO_2)(P(C_6H_5)_3)_3(C_6H_6)$. The calculated molecular weight for this formula is 1171.

Complexes similar to II have been obtained by the

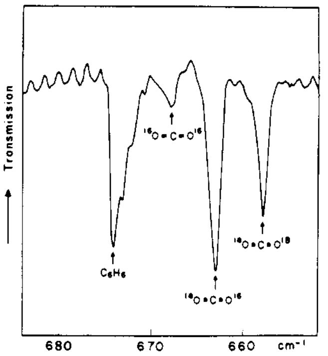

Figure 3. Infrared absorption spectrum of the pyrolyzed gas of ^{18}O-containing complex II.

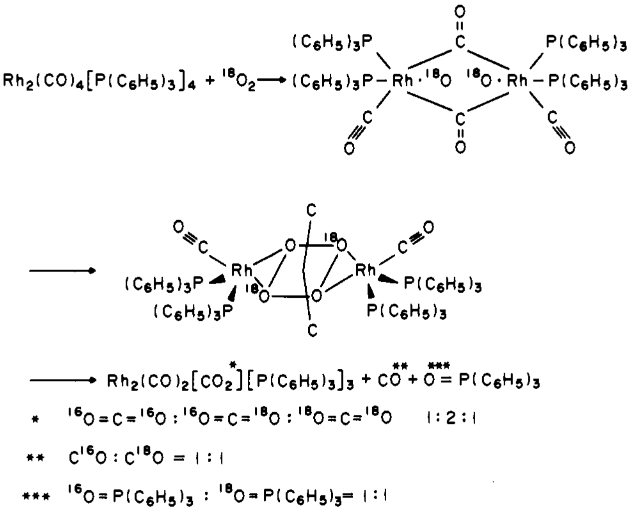

Figure 4. Possible reaction scheme of complex I and molecular oxygen.

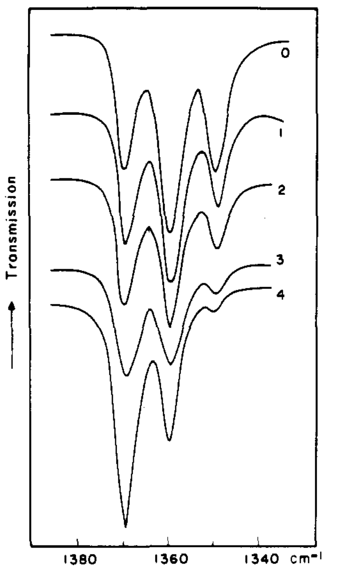

Figure 5. Change in the infrared spectrum of ^{18}O-containing complex II caused by recrystallization from benzene. The number given on each curve indicates how many times the recrystallization procedures of the product were made before the infrared absorption measurement. It is seen here that every recrystallization causes a decrease of ^{18}O content.

reaction of oxygen and the complex I in several solvents other than benzene. The analyses of these complexes (Table II) fit $Rh_2(CO)_2(CO_2)(P(C_6H_5)_3)_3L_n$. Here, L (= benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, or mesitylene) is the solvent in which the reaction of oxygen and complex I takes place. The *n* values were determined by measuring the relative intensities of the signals in the proton magnetic resonance spectra of these complexes. Oxygen analysis also supports the formula of this complex. When complex II is crystallized from aromatic solvents, a definite number of the solvent molecules are brought into the crystal lattice (Table II). The crystals obtained from CH_2Cl_2 seem to be unstable.

Reaction Mechanism

Information is obtained on the mechanism of the reaction of complex I and oxygen by examining the effect of introducing heavy oxygen into the reaction. The infrared spectrum of the pyrolyzed gas of the product of this reaction shows that it contains labeled carbon dioxide, both $^{16}OC^{18}O$ and $C^{18}O_2$ (Figure 3). In addition, from the crystalline residue, ^{18}O-containing triphenylphosphine oxide was also obtained. Therefore complex II is considered to be formed by oxidation by molecular oxygen of CO on rhodium metal in complex I, as follows

$$Rh_2(CO)_4(P(C_6H_5)_3)_4 + O_2 \rightarrow Rh_2(CO)_2(CO_2)P(C_6H_5)_3 + O{=}P(C_6H_5)_3 + CO$$

The relative amounts of $^{16}O{=}C{=}^{16}O$, $^{18}O{=}C{=}^{16}O$, and $^{18}O{=}C{=}^{18}O$ in complex II can be estimated by an infrared absorption measurement of the isotopic complex II (Figure 2). They are found to be about 1, 2, and 1, respectively. On the other hand, the ratio of the amounts of $^{16}O{=}P(C_6H_5)_3 : ^{18}O{=}P(C_6H_5)_3$ is about 1:1. Such a distribution of ^{18}O is explained by considering that there is an intermediate in the reaction in which four equivalent oxygens and two equivalent carbons make an octagon, as illustrated in Figure 4.

Structure of the Coordinated Carbon Dioxide

As has already been stated, three strong absorption bands at 1498, 1368, and 813 cm^{-1} in the infrared spectrum of complex II are assigned to coordinated carbon dioxide (Figures 1 and 2). Carbon dioxide usually absorbs at 2350 and 667 cm^{-1} because of its linear $D_{\infty h}$ form. The fact that the carbon dioxide molecule in the complex II shows three (instead of two) strong bands is taken as indicating that the molecule does not have $D_{\infty h}$ symmetry in this case. The fact that the C–O stretching frequencies of the CO_2 molecule in question are much lower than those in the gas indicates that the C–O bond is weaker in the former than in the latter. This situation is similar to that of carbon disulfide molecule in a complex $Pt(CS_2)(P(C_6H_5)_3)_2$. A C–S stretching frequency of this complex was found at 1157 cm^{-1}.[4] The structure of the CS_2 molecule in this complex was determined by a crystallographic method;[5,6] it was found to have a bent form. Therefore, it is probable that the carbon dioxide molecule in complex II now in question also has a bent form. It may be pointed out here that the CO_2 molecule in the first excited state has been known to take a bent C_{2v} form.[7] When complex II is recrystallized from a solvent, an exchange reaction between the oxygen atoms of the coordinated carbon dioxide molecule and the oxygen atoms in the molecular oxygen in the solvent takes place (Figure 5). This fact indicates that the carbon–oxygen bond in the CO_2 molecule in complex II is in an unusual state (in an activated state, so to say).

Experimental Section

Solvents used in this experiment were dried and distilled and degassed *in vacuo*.

$Rh_4(CO)_{12}$ was prepared from $RhCl_3 \cdot 3H_2O$ by Hieber's[8] method. The reaction product was purified by silica gel column chromatography.

Complex I. In a Schlenk tube 0.2 g of $Rh_4(CO)_{12}$ and 100 ml of benzene solution were placed and 1.0 g of $P(C_6H_5)_3$ was added. After evolution of CO gas, 200 ml of *n*-hexane was added and the mixture cooled. Golden yellow crystals were obtained which decomposed at 104° without melting; ir: 1993 (m), 1977 (s), 1939 (w), 1763 (s), 1739 (s), and 1711 (w) cm^{-1}.

Anal. Calcd for $C_{38}H_{30}O_2P_2Rh$: C, 66.77; H, 4.43; P, 9.25; Rh, 15.05. Found: C, 67.12; H, 4.57; P, 9.06; Rh, 15.00.

Complex II. In an aromatic solvent 0.1 g of complex I was dissolved; the solution cooled to liquid nitrogen temperature, and the system was evacuated. By vacuum line technique, a small amount of oxygen was admitted into the reaction vessel and the reaction mixture was heated to room temperature. After evolution of gas had ended, *n*-hexane was added. Very fine pale yellow needles, which show an extinction under a polarized microscope, were obtained.

Anal. Calcd for $Rh_2(CO)_2(CO_2)(P(C_6H_5)_3)_3C_6H_6$: O, 5.47. Found: O, 6.23.

^{18}O-enriched gas (96.90 atom % ^{18}O) was purchased from Miles Laboratories, Inc., Elkhalt, Ind. The same procedure was followed

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(4) M. C. Baird and G. Wilkinson, *J. Chem. Soc., A*, 865 (1967).

(5) M. C. Baird, G. Hartwell, Jr., R. Mason, A. I. M. Rae, and G. Wilkinson, *Chem. Commun.*, 92 (1967).

(6) T. Kashiwagi, N. Yasuoka, T. Ueki, N. Kasai, and M. Kakudo, *Bull. Chem. Soc. Japan*, **40**, 1998 (1967).

(7) G. Hertzberg, "Electronic Spectra and Electronic Structure of Polyatomic Molecules," 1st ed, D. Van Nostrand Co., Ltd., Princeton, N. J., 1966, p 598.

(8) W. Hieber and H. Lagally, *Z. Anorg. Allg. Chem.*, **251**, 96 (1943).

in the experiment with $^{18}O_2$. The infrared spectra of complex II and its isotopic derivatives are given in Figures 1 and 2 and Table I. In the far-infrared region, a medium band at 343 cm^{-1} is the only one that is not affected by the change of $P(C_6H_5)_3$ to $P(C_6D_5)_3$ and C_6H_6 to C_6D_6. It is shifted to 337 cm^{-1} by incorporation of ^{18}O, and therefore this band may be assigned to the Rh–CO_2 bond stretching mode.

$P(C_6D_5)_3$. Pentadeuteriobromobenzene was prepared by bromination of hexadeuteriobenzene. Ether solution of C_6D_5MgBr, prepared from Mg and C_6D_5Br, was placed in a flask and an ether solution of PCl_3 was added slowly. After vigorous reaction had ended, unreacted reagent was decomposed by 100 ml of HCl. $P(C_6D_5)_3$ was crystallized from the ether layer; yield 40.3% for C_6D_5Br.

Analysis of Carbon Dioxide. In a helium flow 39.25 mg of complex II was pyrolyzed in a quartz tube at 500° for 20 min, and the generated gas was trapped on KOH. The CO_2 content was 4.86 wt %; the calculated value was 3.76 wt % for $Rh_2(CO)_2(CO_2)(P(C_6H_5)_3)_3C_6H_6$. Carbon dioxide was also detected by an F & M Model 80 pyrolyzer gas chromatograph.

Infrared Spectra. Infrared spectra were recorded with a Hitachi Perkin-Elmer Model 225 infrared spectrometer. The wave number calibration was made by the use of known absorption lines of CO, CO_2, and water vapor. Infrared absorptions were observed in the form of Nujol and hexachlorobutadiene mulls.

Molecular Weight Determination. The molecular weight of complex II was determined on a Mechrolab vapor-pressure osmometer. Bibenzyl was used as the reference compound. The observed molecular weight of complex II measured in a benzene solution was 1057; the calculated value for $Rh_2(CO)_2(CO_2)(P(C_6H_5)_3)_3C_6H_6$ is 1171.

Nmr. Nmr spectra were recorded with a Varian HA-100 spectrometer in CD_2Cl_2, C_6D_6, or $CDCl_3$ solutions. Integration of the phenyl protons of $P(C_6H_5)_3$ and methyl protons of the coordinated solvent molecules determined the numbers incorporated in the molecule.

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Stereochemically Nonrigid Organometallic Molecules. XXI.[1] The Crystal and Molecular Structures of Tris(cyclopentadienyl)nitrosylmolybdenum[2]

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Abstract: The crystal and molecular structures of tris(cyclopentadienyl)nitrosylmolybdenum, $(C_5H_5)_3MoNO$, have been determined from 2288 independent, nonzero reflections collected with a counter diffractometer. The compound crystallizes in the monoclinic space group $B2_1/a$ with eight molecules in a unit cell of dimensions $a = 15.425 \pm 0.006$ Å, $b = 7.423 \pm 0.004$ Å, $c = 24.050 \pm 0.007$ Å, and $\beta = 103° 40' \pm 3'$ ($\rho_{obsd} = 1.60$ g cm^{-3}; $\rho_{calcd} = 1.59$ g cm^{-3}). The structure, including hydrogen atoms, was solved from Patterson and electron density maps and refined by least-squares methods to a conventional unweighted R factor of 3.5%. The principal features of the structure are the following. (1) There is an essentially linear (179.2°) Mo–N–O group, with Mo–N = 1.751 (3) Å and N–O = 1.207 (4) Å. The short Mo–N and relatively long N–O distances indicate very strong metal–ligand π bonding. (2) One of the C_5H_5 rings is an exemplary σ or *monohapto* cyclopentadienyl ring. The Mo–C distance is 2.291 (3) Å and the C–C distances (in Å) listed in order from the bound carbon atom around the ring are 1.468 (5), 1.349 (5), 1.442 (6), 1.344 (5), 1.468 (5). (3) The other two rings have almost identical relationships to the metal atom. No simple distinction (such as *pentahapto vs. trihapto*) can be made between them. Around each one, the Mo–C distances go in the following order, where pairs of corresponding bonds to the two rings are listed together: 2.599 (4), 2.682 (5); 2.588 (5), 2.609 (5); 2.343 (5), 2.347 (4); 2.338 (5), 2.324 (3); 2.422 (5), 2.444 (4). These two rings have very different orientations relative to the h^1-C_5H_5 ring, however, and this is most important in considering how to interpret the low-temperature pmr spectrum which has been reported for this fluxional molecule.

In a previous paper in this series,[4] the preparation and a study of the temperature dependence of the proton magnetic resonance spectrum of the molecule $(C_5H_5)_3MoNO$ were described. At room temperature, there is only one narrow line for all 15 protons, but in the temperature range 0 to −50° one ring becomes distinguishable as a *monohapto*[5] cyclopentadienyl group while the other two remain nmr equivalent. Between −60 and −110°, further complexities appear in the spectrum, notably a separation of the resonance due to ten protons into two equally intense resonances separated by ~1 ppm. As noted in the initial report,[4] there are at least two structural

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(1) Part XX: F. A. Cotton and T. J. Marks, *J. Am. Chem. Soc.*, **91**, 1339 (1969).

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(3) Fellow of the Council for Scientific and Humanistic Development, Central University of Venezuela, Caracas, Venezuela.

(4) Part XVIII: F. A. Cotton and P. Legzdins, *J. Am. Chem. Soc.*, **90**, 6232 (1968).

(5) *Cf.* F. A. Cotton, *ibid.*, **90**, 6230 (1968), for an explanation of this notation.