1020. *The Actions of Halogens on Phosphine-substituted Group VI Metal Carbonyls. Part I. The Action of Halogens on Diphosphine-molybdenum and -tungsten Carbonyls*

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The action of halogens on the 1,2-bisdiphenylphosphinoethane (diphos) derivatives [$M(CO)_4$(diphos)] and [$M(CO)_2$(diphos)$_2$] (M = Mo and W) has been investigated. Treatment of one mole of the former with two equivalents of iodine or bromine in dichloromethane yields the compounds [$M(CO)_3$(diphos)X_2], where X = I or Br, and M = Mo or W. These complexes are diamagnetic and non-electrolytes in nitrobenzene, indicating that they are seven-co-ordinate derivatives of Mo^{II} and W^{II}. For the iodides the compounds may be initially isolated as dichloromethane adducts. The bisdiphosphine compounds [$M(CO)_2$(diphos)$_2$] on treatment with three equivalents of iodine give rise to stable paramagnetic, monomeric complexes of Mo^{I} and W^{I}, [$M(CO)_2$(diphos)$_2$]I_3; these complexes are uni-univalent electrolytes and isolation of the perchlorates, [$M(CO)_2$(diphos)$_2$]ClO_4 (M = Mo or W), confirms their formulation as Mo^{I} and W^{I} derivatives.

IN the course of our investigations into the infrared spectra of metal–phosphorus compounds, we have carried out the oxidation with halogens of the phosphine substituted Group VI metal carbonyls [$M(CO)_4$(diphos)], [$M(CO)_2$(diphos)$_2$] where M = Mo or W and diphos = $Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2$, in order to study the effect of variation of oxidation state of the metal on the metal–phosphorus frequency. The action of halogens on these complexes has been studied under (i) controlled or mild conditions, in which a fixed amount of halogen is used, and (ii) forcing conditions, in which an excess of the halogen is employed. In the first case, the retention of carbonyl groups in the product may be anticipated, whereas, in the second, the use of excess of halogen is expected to remove all the carbonyl groups. Treatment of [$Mo(CO)_4$(diphos)] with excess of chlorine or bromine eventually leads to phosphine oxide complexes of the type $\{Mo^{V}OX_3{\cdot}[Ph_2P(O)CH_2CH_2P(O)Ph_2]\}$, where X = Br or Cl. In the case of the tungsten complexes the hexavalent oxidation state seems to be preferred, the reaction yielding $\{W^{VI}O_2X_2{\cdot}[Ph_2P(O)CH_2CH_2P(O)Ph_2]\}$. These complexes will be discussed in a later Paper.

Prévious work on the halogen oxidation of di(tertiary arsine)-substituted Group VI metal carbonyls [1-3] has been carried out mainly under the first set of conditions. It was shown that the oxidation of these complexes with halogens provides a useful method of preparation of compounds in which the metal atom has a low oxidation state and also an unusual stereochemistry. Thus, the compounds [$Mo(CO)_4$(diars)] and [$M(CO)_2$(diars)$_2$], where M = Cr, Mo, or W and diars = *o*-phenylenebisdimethylarsine, react with iodine and bromine to form seven-co-ordinate diamagnetic complexes of bivalent molybdenum [$Mo^{II}(CO)_3$(diars)X_2] for the former and the complexes [$M^{II}(CO)_2$(diars)$_2$X]X for all the metals with the latter compound.

Both [$Mo(CO)_4$(diphos)] and [$W(CO)_4$(diphos)] react with two equivalents of bromine, in dichloromethane at room temperature, with the loss of one mole of carbon monoxide to give the seven-co-ordinate complexes [$Mo(CO)_3$(diphos)Br_2] and [$W(CO)_3$(diphos)Br_2], respectively. These two compounds have similar physical characteristics, being diamagnetic, non-electrolytes in nitrobenzene and have three characteristic C=O stretching frequencies in the infrared region, consistent with the formulation as seven-co-ordinate complexes.

A spectrophotometric titration in dichloromethane indicated that [$Mo(CO)_4$(diphos)]

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[1] H. L. Nigam, R. S. Nyholm, and M. H. B. Stiddard, *J.*, 1960, 1806.

[2] J. Lewis, R. S. Nyholm, C. S. Pande, and M. H. B. Stiddard, *J.*, 1963, 3600.

[3] J. Lewis, R. S. Nyholm, C. S. Pande, S. S. Sandhu, and M. H. B. Stiddard, *J.*, 1964, 3009.

reacted with two equivalents of iodine and measurements by a gas burette indicated the evolution of one mole of carbon monoxide. The initial product of this reaction has an analysis corresponding to the compound $[Mo(CO)_3(diphos)I_2,]CH_2Cl_2$. The dichloromethane can be removed, by heating under high vacuum at 80° for several hours, to yield the orange-brown complex $[Mo(CO)_3(diphos)I_2]$. Like the bromides, these two products were diamagnetic, non-electrolytes in nitrobenzene, and the infrared spectra of the two iodides were identical in the carbonyl stretching region.

For the corresponding tungsten complex $[W(CO)_4(diphos)]$, a spectrophotometric titration indicated that four equivalents of iodine were absorbed and gas-burette measurements taken over approximately an hour after the commencement of the reaction showed that no carbon monoxide had been evolved. This is in agreement with the formulation of the complex as $[W(CO)_4(diphos)I]I_3$ similar to that obtained by reaction of the corresponding diarsine complex with iodine. However no product of this type could be isolated from the reaction mixture but, after several days, bright yellow crystals separated. This solid analysed as $[W(CO)_3(diphos)I_2],CH_2Cl_2$ and the dichloromethane may be removed under high vacuum to give the complex $[W(CO)_3(diphos)I_2]$. This formulation of the product was confirmed by a gas-burette measurement taken over several days, when a volume of gas equivalent to one mole of carbon monoxide was evolved. The compound was found to be diamagnetic and a non-electrolyte in nitrobenzene. The carbon monoxide is obviously lost much less readily in the case of the tungsten compound and this is in agreement with the previous evidence [3] which suggests that there is an increasing tendency for carbon monoxide to be lost on oxidation in the order chromium > molybdenum > tungsten.

The above behaviour would also suggest that there must be a very fine balance of conditions required to favour the formation of either $[W(CO)_3(diphos)I_2]$ or $[W(CO)_4(diphos)I]I_3$. In the case of the corresponding diarsine [2] complex, $[W(CO)_4(diars)]$ reacts with two equivalents of bromine to give $[W(CO)_3(diars)Br_2]$ but with four equivalents of iodine to give $[W(CO)_4(diars)I]I_3$.

On treatment with iodine under the same conditions, the bisdiphosphine dicarbonylmolybdenum, $[Mo(CO)_2(diphos)_2]$, absorbs three equivalents of the halogen without evolution of carbon monoxide to yield a red compound which analyses as $[Mo(CO)_2(diphos)_2I_3]$. This complex is paramagnetic ($\mu_{eff} = 1{\cdot}66$ B.M.). The conductivity data in nitrobenzene have been analysed according to the method of Feltham and Hayter [4] and are consistent with its formulation as a monomeric complex behaving as a uni-univalent electrolyte. On this basis the compound may be formulated as either an octahedral tri-iodide derivative of molybdenum(I), $[Mo(CO)_2(diphos)_2]I_3$, or an eight-co-ordinate derivative of molybdenum(III), $[Mo(CO)_2(diphos)_2I_2]I$. Only one strong carbonyl stretching frequency is observed, at 1864 cm.$^{-1}$, indicating that the two carbonyl groups are situated in positions *trans* to each other. The low value of this frequency would favour the formulation of the complex as a molybdenum(I) derivative.

Properties of halogenocarbonylmetal complexes

Complex	Colour	Mol. conductivity (Ω^{-1} cm.^{2}) (10^{-3}M in PhNO$_2$)	Magnetism (μ_{eff} of solid at 20°)	C=O Stretching frequencies (cm.$^{-1}$) in hexachlorobutadiene		
$[Mo(CO)_3(diphos)I_2],CH_2Cl_2$	Orange-yellow	2·8	Diamag.	2036	1986	1925
$[Mo(CO)_3(diphos)I_2]$	Orange-brown	0·9	Diamag.	2035	1984	1924
$[Mo(CO)_3(diphos)Br_2]$	Yellow	0·8	Diamag.	2050	1967	1904
$[W(CO)_3(diphos)I_2],CH_2Cl_2$	Bright yellow	1·3	Diamag.	2026	1970	1911
$[W(CO)_3(diphos)I_2]$	Yellow	0·7	Diamag.	2029	1971	1912
$[W(CO)_3(diphos)Br_2]$	Yellow	0·7	Diamag.	2044	1955	1892
$[Mo(CO)_2(diphos)_2]I_3$	Red	25·9	1·66	1864		
$[Mo(CO)_2(diphos)_2]ClO_4$	Salmon-pink	27·3	1·61	1865		
$[W(CO)_2(diphos)_2]I_3$	Red	26·8	1·86	1853		
$[W(CO)_2(diphos)_2]ClO_4$	Orange	—	—	1855		

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[4] R. D. Feltham and R. G. Hayter, *J.*, 1964, 4587.

The results of spectrophotometric and conductometric titrations in this system are in agreement with this suggestion. A spectrophotometric titration of [$Mo(CO)_2(diphos)_2$] with iodine in dichloromethane, using the absorption at 500 mμ (the position of a maximum in the iodine spectrum) indicated the formation of a 1 : 1 intermediate. Subsequent reaction of this to give the final 1 : 3 adduct was also indicated in this titration. The form of the spectrophotometric curve, however, was unusual (Figure 1). This is due to the fact that, for the 1 : 1 complex, a maximum occurs in the absorption spectrum at 480 mμ. Addition of iodine causes a build-up in this maximum to the 1 : 1 ratio and a subsequent addition of iodine causes a decrease in the intensity of this band as the 1 : 3 adduct is formed. In the conductometric titration of iodine with the complex, in nitrobenzene (Figure 2) the conductivity was found to increase the 1 : 1 ratio and remain constant during the addition of the next molecule of iodine, as anticipated for the formation of the tri-iodide ion. Subsequent addition of iodine causes a rise in the conductivity which is parallelled by addition of iodine to the 1 : 3 adduct. The formulation of this compound as a derivative of molybdenum(I) has been confirmed by the isolation of the perchlorate, [$Mo(CO)_2(diphos)_2$]ClO_4, from reaction of the tri-iodide with silver perchlorate in tetrahydrofuran. The perchlorate complex is paramagnetic (μ_{eff} = 1·61 B.M.), a uni-univalent electrolyte in nitrobenzene behaving as a monomeric species (see ref. 4).

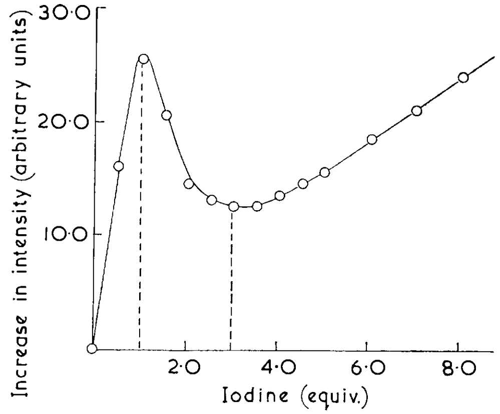

FIGURE 1. Spectrophotometric titration of [$Mo(CO)_2(diphos)_2$] with iodine in CH_2Cl_2 (λ = 500 mμ; 1 cm. cell)

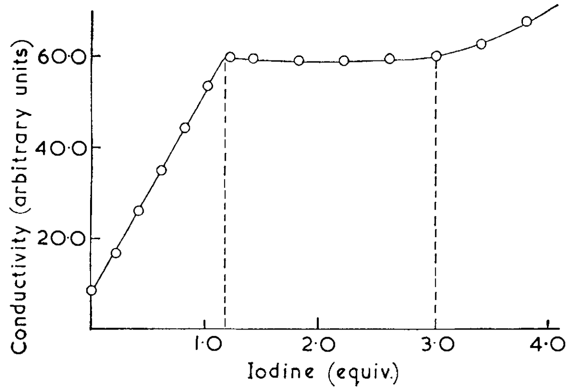

FIGURE 2. Conductometric titration of 1·0 × 10^{-3} M [$Mo(CO)_2(diphos)_2$] against iodine in nitrobenzene

The dicarbonyltungsten complex, [$W(CO)_2(diphos)_2$], reacts with iodine in the same manner to produce the red compound [$W(CO)_2(diphos)_2$]I_3, with similar properties to the molybdenum tri-iodide complex. A parallel behaviour to that observed for the molybdenum system was observed in the spectrophotometric and conductometric titrations of the neutral complex with iodine. Reaction of the tri-iodide with silver perchlorate in tetrahydrofuran produced an orange complex, the infrared spectrum of which indicated the formulation of $[W(CO)_2(diphos)_2]ClO_4$. However, consistent analyses could not be obtained for this compound and the magnetic moment of different samples varied over the range 1·3—1·5 B.M. The moment is lower than the tri-iodide complex and it appears that some decomposition is occurring. This is in keeping with the fact that the stability of low oxidation states is less for tungsten than for molybdenum.

The isolation of stable mononuclear derivatives of molybdenum(I) and tungsten(I) is unusual. Mononuclear molybdenum(I) and tungsten(I) complexes have been prepared previously as $[M(\pi\text{-}C_6H_6)_2]^+$ (M = Mo or W),[5] and $[Mo(\pi\text{-}C_5H_5)(\pi\text{-}C_6H_6)]$,[6] but both of these are readily oxidised in air, in marked contrast to the behaviour of the iodides isolated in this study. The binuclear complexes $[(\pi\text{-}C_5H_5)M(CO)_3]_2$ (M = Mo or W),[7] may be also formally considered as examples of the oxidation state molybdenum(I) and tungsten(I). As has been discussed previously[8] there is a great tendency for elements of the early transition series, in low oxidation states towards dimerisation, with metal–metal bond formation and attainment of a complete *d*-shell configuration. However the d^5-configuration provides a unique example of a stable paramagnetic carbonyl compound, in vanadium hexacarbonyl. In this instance, substitution of the carbonyl groups by phosphine can lead to the formation of diamagnetic dimeric compounds.[9] The general factors concerned in monomer–dimer systems of this type have been discussed for the corresponding d^7-system.[10] However, dimer formation in the d^5-system requires seven-co-ordination for the central metal atom and, in addition to the positive charge on the species, it is obvious that steric factors may play a much more important role in these systems than in the corresponding d^7-systems. It is of interest to note that for the phosphinecarbonyl derivatives of molybdenum(I) and tungsten(I) reported here, the infrared spectra indicate that the two carbonyl groups are in the *trans* arrangement. It is generally found that, in complexes of this type, maximum π-bonding with the metal and stability is associated with a *cis* distribution. The stabilisation of this arrangement may be correlated, however, with the lower steric interaction between the phosphine groups in the *trans* arrangement and this steric effect may, in part, explain the stability of the monomeric over the dimeric species. We are now investigating the variation in the nature of the phosphine on the monomer–dimer equilibrium in these systems.

EXPERIMENTAL

Di-iodotricarbonylmonobisdiphenylphosphinoethanemolybdenum(II)*–Dichloromethane Adduct.* —The complex $[Mo(CO)_4(diphos)]$ (0·61 g.) in dichloromethane (40 ml.) was treated with iodine (0·26 g.) (*i.e.*, Mo : I_2 = 1 : 1) in dichloromethane (30 ml.) for 30 min. under dry nitrogen with rapid stirring at room temperature. One mole of carbon monoxide per mole of complex was liberated and the *compound* $[Mo(CO)_3(diphos)I_2],CH_2Cl_2$ (0·72 g.) formed orange-yellow crystals, m. p. 204—206° (decomp.), after removal of solvent under vacuum and addition of light petroleum; it was washed with light petroleum and dried *in vacuo* (Found: C, 39·4; H, 3·0; Cl, 7·2; I, 27·5; P, 6·7. $C_{30}H_{26}Cl_2I_2MoO_3P_2$ requires C, 39·3; H, 2·8; Cl, 7·7; I, 27·7; P, 6·8%). The compound is stable in air, soluble in acetone, chloroform, dichloromethane, and nitrobenzene, and insoluble in all other common organic solvents.

Di-iodotricarbonylmonobisdiphenylphosphinoethanemolybdenum(II).—On heating the foregoing adduct at 80°/0·01 mm. for several hours, a loss in weight corresponding to the loss of one mole of dichloromethane occurred, giving the *complex* $[Mo(CO)_3(diphos)I_2]$ as an orange-brown solid, m. p. 208—209° (decomp.) (Found: C, 41·6; H, 2·9; I, 30·4; P, 7·4. $C_{29}H_{24}I_2MoO_3P_2$ requires C, 41·8; H, 2·9; I, 30·5; P, 7·5%). The compound has identical properties with the dichloromethane adduct.

[5] E. O. Fischer, F. Scherer, and H. O. Stahl, *Chem. Ber.*, 1960, **93**, 2065.
[6] E. O. Fischer and F. J. Kohl, *Angew. Chem.*, 1964, **76**, 98.
[7] G. Wilkinson, *J. Amer. Chem. Soc.*, 1954, **76**, 209.
[8] J. Lewis and R. S. Nyholm, *Sci. Progr.*, 1964, **52**, 557.
[9] W. Hieber and E. Winter, *Chem. Ber.*, 1964, **97**, 1037.
[10] C. E. Coffey, J. Lewis, and R. S. Nyholm, *J.*, 1964, 1741.

Dibromotricarbonylmonobisphenylphosphinoethanemolybdenum(II).—The complex [Mo(CO)$_4$(diphos)] (0·61 g.) in dichloromethane (50 ml.) was treated with bromine (0·16 g.) (*i.e.*, Mo : Br$_2$ = 1 : 1) in dichloromethane (25 ml.) for 40 min. under dry nitrogen with efficient stirring to prevent local concentrations of the halogen. One mole of carbon monoxide was liberated. The volume of the solution was reduced under vacuum and light petroleum added, giving the *compound* [Mo(CO)$_3$(diphos)Br$_2$] (0·32 g.) as yellow crystals, m. p. 216—218°. It was washed with light petroleum and dried *in vacuo* (Found: C, 47·1; H, 3·4; Br, 21·8; P, 8·5. $C_{29}H_{24}Br_2MoO_3P_2$ requires C, 47·2; H, 3·3; Br, 21·7; P, 8·4%). The compound is reasonably stable in air but decomposes over a period of weeks. It is soluble in acetone, chloroform, dichloromethane, and nitrobenzene.

Di-iodotricarbonylmonobisdiphenylphosphinoethanetungsten(II).—*Dichloromethane Adduct*.—The complex [W(CO)$_4$(diphos)] (0·70 g.) in dichloromethane (40 ml.) was treated with iodine (0·26 g.) in dichloromethane (30 ml.) as above. One mole of carbon monoxide was liberated during the course of a day, and the *adduct* [W(CO)$_3$(diphos)I$_2$],CH$_2$Cl$_2$ (0·48 g.) crystallised slowly at 0° as bright yellow crystals, m. p. 235—237°, after the addition of light petroleum; it was washed with light petroleum and dried *in vacuo* (Found: C, 35·8; H, 2·6; Cl, 7·1; I, 25·5; P, 6·3. $C_{30}H_{26}Cl_2I_2O_3P_2W$ requires C, 35·8; H, 2·6; Cl, 7·1; I, 25·3; P, 6·2%). The compound is quite stable in air and its solubility properties are similar to those of the molybdenum analogue.

Di-iodotricarbonylmonobisdiphenylphosphinoethanetungsten(II).—As for the molybdenum complex, this was prepared by heating the dichloromethane adduct under high vacuum at 80° for several hours. Again a loss in weight corresponding to the loss of one mole of dichloromethane occurred, producing the *compound* [W(CO)$_3$(diphos)I$_2$] as yellow crystals, m. p. 236—238° (decomp.) (Found: C, 37·7; H, 2·6; I, 27·5; P, 6·7. $C_{29}H_{24}I_2O_3P_2W$ requires C, 37·8; H, 2·6; I, 27·5; P, 6·7%). Its properties are similar to those of the dichloromethane adduct.

Dibromotricarbonylmonobisdiphenylphosphinoethanetungsten(II).—The tungsten complex [W(CO)$_4$(diphos)] (0·70 g.) in dichloromethane (50 ml.) was treated with bromine (0·16 g.) in dichloromethane (25 ml.) as above. One mole of carbon monoxide was liberated and the *dibromide* [W(CO)$_3$(diphos)Br$_2$] (0·56 g.) formed yellow crystals, m. p. 210—211° (decomp.), after the addition of light petroleum; it was washed with light petroleum and dried *in vacuo* (Found: C, 42·3; H, 3·1; Br, 19·6; P, 7·5. $C_{29}H_{24}Br_2O_3P_2W$ requires C, 42·1; H, 2·9; Br, 19·4; P, 7·5%). The compound is stable in air; its properties are similar to those of the molybdenum complex.

Dicarbonylbisbisdiphenylphosphinoethanemolybdenum(I) *Tri-iodide*.—A suspension of the complex [Mo(CO)$_2$(diphos)$_2$] (0·95 g.) in dichloromethane (75 ml.) was treated with iodine (0·38 g.) (*i.e.*, Mo : I$_2$ = 1 : 1·5) in dichloromethane (35 ml.) with rapid stirring under dry nitrogen at room temperature. No carbon monoxide was liberated and the *tri-iodide* [Mo(CO)$_2$(diphos)$_2$]I$_3$ formed red crystals, m. p. 201—202° (decomp.), after addition of light petroleum to the red solution; it was washed with light petroleum and dried *in vacuo* (Found: C, 48·7; H, 3·5; I, 28·9; P, 9·3. $C_{54}H_{48}I_3MoO_2P_4$ requires C, 48·8; H, 3·6; I, 28·7; P, 9·3%). The compound is stable in air, appreciably less soluble in organic solvents than the complexes containing just one phosphine grouping, and only very sparingly soluble in acetone, chloroform, and dichloromethane.

Dicarbonylbisbisdiphenylphosphinoethanemolybdenum(I) *Perchlorate*.—A suspension of the complex [Mo(CO)$_2$(diphos)$_2$]I$_3$ (0·23 g.) in tetrahydrofuran (40 ml.) was shaken with silver perchlorate (0·12 g.) in tetrahydrofuran (5 ml.) for 1 hr. under dry nitrogen at room temperature. After filtration of the precipitated silver iodide the pink solution was concentrated to 15 ml. and the compound [Mo(CO)$_2$(diphos)$_2$]ClO$_4$ crystallised slowly as salmon-pink crystals, m. p. 160—161° (decomp.), after the addition of light petroleum; it was washed with light petroleum and dried *in vacuo* (Found: C, 62·3; H, 4·5; Cl, 3·4; P, 11·7. $C_{54}H_{48}ClMoO_6P_4$ requires C, 61·8; H, 4·6; Cl, 3·4; P, 11·8%). The complex is stable in air and very soluble in chloroform, dichloromethane, tetrahydrofuran, acetone, and nitrobenzene.

Dicarbonylbisbisdiphenylphosphinoethanetungsten(I) *Tri-iodide*.—A suspension of the complex [W(CO)$_2$(diphos)$_2$] (0·69 g.) in dichloromethane (75 ml.) was treated with iodine (0·26 g.) in dichloromethane (35 ml.) as above. No carbon monoxide was liberated and the *tri-iodide* [W(CO)$_2$(diphos)$_2$]I$_3$, m. p. 216—217° (decomp.), crystallised from the red solution after the addition of light petroleum; it was washed with light petroleum and dried *in vacuo* (Found: C, 45·6; H, 3·4; I, 27·0; P, 8·6. $C_{54}H_{48}I_3O_2P_4W$ requires C, 45·7; H, 3·4; I, 26·9; P, 8·8%).

The compound is stable in air and its physical properties are very similar to the molybdenum analogue.

Spectrophotometric Titrations.—A 10^{-3}M-solution of the halogen in dichloromethane was titrated against a 10^{-3}M-solution of the phosphine-substituted carbonyl in dichloromethane. The concentrations of free halogen were followed by measuring the intensity of the absorption at 500 mμ. The plot of change of intensity against halogen added showed a change of slope at a position corresponding to the number of equivalents of halogen reacting.

Measurement of Carbon Monoxide Evolved on Reaction with Halogen.—Measurement of the volumes of carbon monoxide evolved on the reaction of halogens with the phosphine-substituted metal carbonyls was carried out in a gas burette of the usual type. The reaction was caused by addition of the complex in a small tube to the halogen solution. The amount of complex used was adjusted to give an evolution of *ca.* 7—8 ml. carbon monoxide and was generally *ca.* 0·20—0·25 g.

Infrared Spectra.—These were measured on a Perkin-Elmer 221 double-beam spectrometer with a sodium chloride prism.

Analyses.—These were performed by the Max Planck Institute, Ruhr, Germany. Halogen analyses were also performed gravimetrically by precipitation as the appropriate silver salt. The complex was decomposed by mixing with solid silver nitrate and then digesting with concentrated nitric acid.

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