

AF EDHR-64-9

AFOSR 65-0237

JAN 27 1965

AD611382

HYDRIDO-COMPLEXES OF TRANSITION METALS.
PART I. HYDRIDO-COMPLEXES OF RHODIUM(I),
COBALT(I), AND COBALT(III)

REPRODUCTION IN WHOLE OR
IN PART IS PERMITTED FOR ANY
PURPOSE OF THE U.S. GOVERNMENT

BY
A. SACCO
AND
R. UGO

UNIVERSITA' di MILANO
ISTITUTO DI CHIMICA GENERALE
MILANO - Via C. Saldini, 50 - Città degli Studi
Telef. 292.163 - 230.139

COPY	2	OF	3	✓
HARD COPY	\$.	—		
MICROFICHE	\$.	—		

6P

Preprinted from the
Journal of the Chemical Society, September 1964, pages 3274—3278.

ARCHIVE COPY

621. *Hydrido-complexes of Transition Metals. Part I. Hydrido-complexes of Rhodium(I), Cobalt(I), and Cobalt(III).*

By A. SACCO and R. UGO.

The preparation and properties are described of complex-salts of rhodium(I), $[\text{Rh}(\text{C}_2\text{H}_4(\text{PPh}_2)_2)_2]\text{X}$ ($\text{X} = \text{Cl}, \text{ClO}_4, \text{BPh}_4$). From these compounds, a very stable hydrido-complex of rhodium(I), $[\text{RhH}(\text{C}_2\text{H}_4(\text{PPh}_2)_2)_2]$, has been prepared by reduction with lithium aluminium hydride or sodium borohydride. The product of the reaction between $[\text{CoBr}_2(\text{C}_2\text{H}_4(\text{PPh}_2)_2)_2]$ and sodium borohydride, previously described as a derivative of cobalt(0), is shown to be a hydrido-complex of cobalt(I), $[\text{CoH}(\text{C}_2\text{H}_4(\text{PPh}_2)_2)_2]$. This formula is supported by the diamagnetism of the compound, by its infrared spectrum, and by its reaction with carbon tetrachloride to give chloroform. On the grounds of their dipole moments (*ca.* 3—4D) and of their isomorphism with $[\text{Ni}(\text{C}_2\text{H}_4(\text{PPh}_2)_2)_2]$, a non-orthogonal structure for these hydrido-complexes of rhodium and cobalt is suggested. The hydrido-complexes of cobalt(I) behaves like a Lewis base, giving with perchloric acid the hydrido-complex $[\text{CoH}(\text{C}_2\text{H}_4(\text{PPh}_2)_2)_2]\text{ClO}_4$.

A number of stable hydrido-complexes of transition metals of general formula $[\text{MH}_2\text{X}_2\text{L}_2]$, where X is an anionic ligand and L is a tertiary phosphine or arsine, have been prepared in the last few years.¹ Among the metals of the cobalt group, many very stable derivatives of iridium,² and only a few of rhodium,³ are known. The only known hydrido-complex of cobalt, stabilised by a tertiary phosphine, is $[\text{CoH}(\text{C}_2\text{H}_4(\text{PPh}_2)_2)_2]$, which has been prepared in these laboratories⁴ by reduction of $[\text{CoBr}_2(\text{C}_2\text{H}_4(\text{PPh}_2)_2)_2]$ with lithium aluminium hydride in tetrahydrofuran; $[\text{CoD}(\text{C}_2\text{H}_4(\text{PPh}_2)_2)_2]$ was similarly prepared by use of lithium aluminium deuteride.⁴

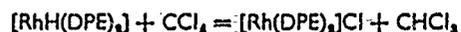
In this Paper, we describe the preparation and properties of (a) some complex-salts of rhodium(I), $[\text{Rh}(\text{DPE})_2]\text{X}$ ($\text{DPE} = 1,2$ -bis(diphenylphosphino)ethane; $\text{X} = \text{Cl}, \text{ClO}_4, \text{BPh}_4$); (b) a new, very stable hydrido-complex of rhodium(I), $[\text{RhH}(\text{DPE})_2]$; (c) a hydrido-complex of cobalt(I), $[\text{CoH}(\text{DPE})_2]$, obtained by reaction between $[\text{CoBr}_2(\text{DPE})_2]$ and sodium borohydride (previously described⁵ as giving a cobalt(0) derivative), and (d) a hydrido-complex of cobalt(III), obtained from $[\text{CoH}(\text{DPE})_2]$ by reaction with perchloric acid.

Rhodium Derivatives.—The compound $[\text{Rh}(\text{DPE})_2]\text{Cl}$ is easily prepared from $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ and the diphosphine in benzene. It is a stable, yellow, crystalline substance, soluble in polar organic solvents, in which it is ionised, and insoluble in hydrocarbons. The corresponding perchlorate and tetraphenylborate are readily obtained by exchange in alcoholic solution.

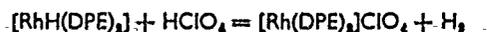
The hydrido-complex of rhodium(I) is obtained by reduction of $[\text{Rh}(\text{DPE})_2]\text{Cl}$ with lithium aluminium hydride in tetrahydrofuran, or with sodium borohydride in ethanol. It is an orange, crystalline compound, rather soluble in benzene, but insoluble in alcohols and light petroleum. It shows considerable thermal stability (decomp. 280°), but is rapidly oxidised by air.

The deuterido-complex is obtained in a similar way, by using lithium aluminium deuteride in tetrahydrofuran, and can be recrystallised by adding ethanol to its benzene solution without any detectable exchange occurring.

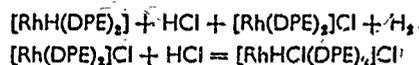
Reactions. The hydrido-complex of rhodium(I) reacts at room temperature with carbon tetrachloride:



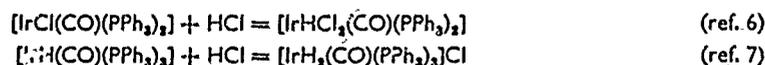
and with perchloric acid, in aqueous ethanol, hydrogen being evolved:



On treating the hydride with hydrogen chloride under the same conditions, hydrogen is still evolved, with a molar ratio, hydrogen: complex, of 1:1, but the product of the reaction contains two atoms of chlorine per atom of rhodium and behaves as a uni-univalent electrolyte. This compound is diamagnetic and has a weak infrared band in the region of the metal-hydrogen stretching vibrations, *i.e.*, at 2110 cm^{-1} . The same compound is also obtained by treating $[\text{Rh}(\text{DPE})_2]\text{Cl}$ with hydrogen chloride in ethanol, under nitrogen, and we therefore consider it to be a hydrido-complex of trivalent rhodium, formed as follows:



Although further studies will be undertaken to confirm this formulation, it is supported by the analogous addition of hydrogen chloride to iridium(I) complexes:



and to the platinum(II) complex⁸ $[\text{PtHCl}(\text{PEt}_3)_2]$, to give $[\text{PtH}_2\text{Cl}_2(\text{PEt}_3)_2]$.

Cobalt Derivatives.—By reaction of $[\text{CoBr}_2(\text{DPE})_2]$ with sodium borohydride, either in absolute or in aqueous ethanol, a red crystalline compound is obtained, which, both before and after recrystallisation from benzene-ethanol or dimethylformamide, shows an infrared spectrum, a decomposition point, and magnetic and chemical behaviour exactly similar to that of the compound obtained⁴ by reduction of $[\text{CoBr}_2(\text{DPE})_2]$ with lithium aluminium hydride, and shown to be the hydrido-complex $[\text{CoH}(\text{DPE})_2]$.

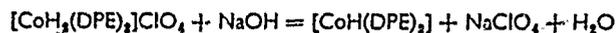
This compound is very rapidly oxidised by air, particularly in solution. In those of our preparations carried out under nitrogen contaminated with 2–3% of oxygen, we obtained samples with magnetic moments ranging from 0.8 to 1.5 B.M.; only when great care was taken to exclude oxygen, were diamagnetic samples of the compound obtained. Therefore, we think that the magnetic moment previously found⁵ for the compound, obtained by the same reaction could have been due to a slight contamination of the product.

Reactions. The hydrido-complex of cobalt(I) reacts with carbon tetrachloride, giving chloroform, but unlike the corresponding rhodium compound, no hydrogen is evolved on reaction with acids.

With perchloric acid, it gives a yellow, diamagnetic hydrido-complex of cobalt(III):



This cobalt(III) complex is stable in air over a period of days, is slightly soluble in ethanol and in tetrahydrofuran, but insoluble in hydrocarbons, and is a uni-univalent electrolyte in nitrobenzene. On treatment with an alcoholic or an aqueous solution of sodium hydroxide, it gives the starting hydrido-complex of cobalt(I):



The corresponding deuterido-complex is obtained from the deuterido-complex of cobalt(I) and deuterated perchloric acid in deuterated ethanol. On reaction with an ethanolic solution of sodium hydroxide, it gives the deuterido-complex of cobalt(I), with no exchange.

Infrared Spectra.—The spectra of some rhodium(I), cobalt(I), and nickel(0) complexes are shown in the Figure. The hydrido-complex of rhodium(I) has a strong sharp infrared band at 1902 cm^{-1} due to the metal-hydrogen stretching vibration, the corresponding deuterido-complex has a strong sharp band at 1465 cm^{-1} (ratio of hydride to deuteride stretching frequencies = 1.39:1). Moreover, the hydrido-complex has a band at 625 cm^{-1} , which is absent for the deuterido-complex, and which we tentatively assign to the bending mode $\delta(\text{Rh-H})$.

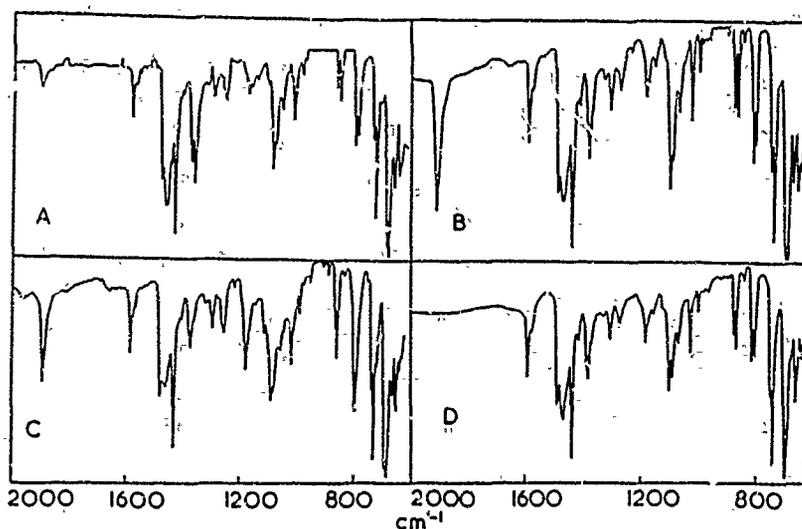
The hydrido-complex of cobalt(I) has a band of medium intensity at 1884 cm^{-1} , ascribable, by comparison with the spectrum of the corresponding deuteride,⁴ to the stretching mode $\nu(\text{Co-H})$.

The increase in M-H stretching frequency on going from cobalt to rhodium is in agreement with the increase of M-H bond strength generally observed on passing from the light to the heavy elements.

The hydrido-complex of cobalt(III) has two bands of medium intensity at 1940 and 1985 cm^{-1} , on the basis of which we assign an *cis* octahedral configuration to it. The corresponding deuterido-complex has only one band at 1400 cm^{-1} ascribable to the stretching mode $\nu(\text{Co-D})$, the second band is most probably hidden by the strong band of the ligand at 1435 cm^{-1} .

Dipole Moments and Structure.—The hydrido-complex of rhodium(I) in benzene has a dipole moment of 4.35 D (assuming ${}_A P = 0$) or 4.03 D (assuming ${}_A P = 0.20\text{ }_R P$). The hydrido-complex of cobalt(I) has a moment of 3.50 D (${}_A P = 0$) or 3.08 D (${}_A P = 0.20\text{ }_R P$).

The dipole moments ($4.2\text{--}4.9\text{ D}$) obtained by Chatt¹ for the hydrido-complexes of the type *trans*- $[\text{PtHCl}(\text{PR}_3)_2]$ and *trans*- $[\text{MHCl}(\text{C}_2\text{H}_4(\text{PEt}_2)_2)_2]$ ($M = \text{Fe, Ru, Os}$) indicate



Infrared spectra: (A) $\text{RhD}(\text{DPE})_2$; (B) $\text{RhH}(\text{DPE})_2$; (C) $\text{CoH}(\text{DPE})_2$; (D) $\text{Ni}(\text{DPE})_2$.

that the metal-hydrogen bond-moment is less than 2 D , and, owing to the increased negative character of the *trans*-halogen under the influence of the hydride ligand, is probably much less than this value. Therefore, for the hydrido-complexes of rhodium(I) and cobalt(I) studied here, a tetragonal structure, with the four phosphorus atoms in the same plane as the metal atom, can be excluded. The dipole moments of these hydrido-complexes and the isomorphism found between $[\text{CoH}(\text{DPE})_2]$, $[\text{RhH}(\text{DPE})_2]$, and $[\text{Ni}(\text{DPE})_2]$ indicate a distorted tetrahedral arrangement of the phosphorus atoms around the central metal atom, with the hydrogen atom situated along a trigonal axis, *i.e.*, a structure similar to that proposed for the cobalt tetracarbonyl hydride.⁹

If the suggested structure could be confirmed by an X-ray study, these compounds would represent the first example of very stable hydrido-complexes having a non-orthogonal configuration.

Nuclear Magnetic Resonance Spectra.—The spectra of the hydrido-complexes in deuterated benzene did not show any band assignable to the proton resonance of the hydridic hydrogen, probably for one or more the following reasons: poor solubility of the compounds in benzene; inadequate sensitivity of the spectrometer; and splitting of the hydrogen band into a number of very weak bands, owing to the interaction of the proton with the phosphorus nuclei of spin $\frac{1}{2}$. The very sharp bands shown by the C_6H_5 and

CH_2 groups of the ligand confirm the diamagnetism of the compounds, independently observed by means of the Gouy method.

EXPERIMENTAL

The diphosphine $(\text{CH}_2\text{-PPh}_2)_2$ was prepared as described by Chatt and Hart.¹⁰ The hydrido-complexes were manipulated in an atmosphere of dry nitrogen, and samples for m. p. determination were contained in evacuated tubes. Infrared spectra were measured on Nujol mulls, using the Perkin-Elmer 237 spectrometer. Nuclear magnetic resonance spectra were measured with the Varian 4310 C spectrometer.

Di-(1,2-bisdiphenylphosphinoethane)rhodium(I) Chloride, $[\text{Rh}(\text{C}_2\text{H}_4(\text{PPh}_2)_2)_2]\text{Cl}$.—A solution of the diphosphine (3.1 g., 2 mol.) in benzene (20 c.c.) was added to a solution of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (0.7 g., 1 mol.) in benzene (10 c.c.). The resulting yellow precipitate was washed with warm benzene and dried. The complex is diamagnetic, soluble in chloroform, methylene chloride, methanol, ethanol, and acetone, but insoluble in benzene and light petroleum, and has m. p. 215° (Found: C, 66.7; H, 5.2; Cl, 3.8. $\text{C}_{52}\text{H}_{48}\text{ClP}_4\text{Rh}$ requires C, 66.8; H, 5.2; Cl, 3.8%); molar conductance (10^{-3}M -solution in nitrobenzene at 28°), 24.0 ohm⁻¹.

Di-(1,2-bisdiphenylphosphinoethane)rhodium(I) Perchlorate, $[\text{Rh}(\text{C}_2\text{H}_4(\text{PPh}_2)_2)_2]\text{ClO}_4$.—A solution of the above chloride, in ethanol, was treated with an ethanolic solution of sodium perchlorate. The resulting golden-yellow precipitate was washed with ethanol and dried; it had m. p. 282° (Found: C, 61.75; H, 4.7; Cl, 3.6. $\text{C}_{52}\text{H}_{48}\text{ClO}_4\text{P}_4\text{Rh}$ requires C, 62.5; H, 4.8; Cl, 3.55%); molar conductance (10^{-3}M -solution in nitrobenzene at 25°), 21.6 ohm⁻¹.

Di-(1,2-bisdiphenylphosphinoethane)rhodium(I) Tetraphenylborate, $[\text{Rh}(\text{C}_2\text{H}_4(\text{PPh}_2)_2)_2]\text{BPh}_4$.—This complex was prepared in a similar manner to the perchlorate, except that sodium tetraphenylborate was used instead of sodium perchlorate. It is a light yellow powder, m. p. 246° (Found: C, 75.3; H, 5.8. $\text{C}_{76}\text{H}_{68}\text{BP}_4\text{Rh}$ requires C, 74.9; H, 5.6%); molar conductance (10^{-3}M -solution in nitrobenzene at 25°), 15.7 ohm⁻¹.

Hydridodi-(1,2-bisdiphenylphosphinoethane)rhodium(I), $[\text{RhH}(\text{C}_2\text{H}_4(\text{PPh}_2)_2)_2]$.—(a) A solution of $[\text{Rh}(\text{DPE})_2]\text{Cl}$ (2.0 g., 1 mol.) in ethanol (40 c.c.) was treated with a solution of sodium borohydride (0.24 g., 3 mol.) in ethanol (30 c.c.) under nitrogen. The resulting crystalline precipitate was filtered off, dried, and crystallised from benzene, by adding ethanol, to give diamagnetic orange plates, decomp. 280°, soluble in benzene, but insoluble in ethanol, methanol, and light petroleum (Found: C, 69.25; H, 5.6; P, 14.1. $\text{C}_{52}\text{H}_{48}\text{P}_4\text{Rh}$ requires C, 69.3; H, 5.5; P, 13.75%).

(b) A solution of $[\text{Rh}(\text{DPE})_2]\text{Cl}$ (1.0 g., 1 mol.) in tetrahydrofuran (30 c.c.) was treated with an excess of lithium aluminium hydride in tetrahydrofuran under nitrogen. The original yellow solution rapidly became orange, and ethanol was then slowly added until effervescence ceased. The solvent was removed under reduced pressure (6 mm.), and from the benzene-soluble portion of the residue, the complex was precipitated with ethanol; it was identified by means of its infrared spectrum.

Deuteridodi-(1,2-bisdiphenylphosphinoethane)rhodium(I) was similarly prepared, in tetrahydrofuran, from $[\text{Rh}(\text{DPE})_2]\text{Cl}$ and lithium aluminium deuteride.

Hydridodi-(1,2-bisdiphenylphosphinoethane)cobalt(I), $[\text{CoH}(\text{C}_2\text{H}_4(\text{PPh}_2)_2)_2]$.—This was prepared from dibromodi-(1,2-bisdiphenylphosphinoethane)cobalt and sodium borohydride (i) in absolute ethanol, as for the corresponding rhodium derivative, and (ii) as according to Chatt,⁵ in 3:1 ethanol-water solution. It formed diamagnetic red plates, decomp. 280° (Found: C, 72.8; H, 5.9; P, 14.5. Calc. for $\text{C}_{52}\text{H}_{48}\text{CoP}_4$: C, 72.9; H, 5.8; P, 14.5%).

Reactions of the Hydrido-complex of Rhodium(I).—(1) *Reaction with perchloric acid*. The hydrido-complex (0.1374 g.) was treated, in an evacuated apparatus, with a solution (5 c.c.) of 1M-perchloric acid in 4:1 ethanol-water, and the evolved gas (4.00 c.c. at 20° and 750 mm.) was collected. The molar ratio hydrogen:complex was 1.06:1. The solid residue was filtered off, washed with ethanol, and dried, and was identified as di-(1,2-bisdiphenylphosphinoethane)rhodium(I) perchlorate by means of its infrared spectrum, m. p., and analysis (Found: Cl, 3.72%).

(2) *Reaction with hydrogen chloride*. The hydrido-complex (0.1312 g.) was treated, in an evacuated apparatus, with a solution (5 c.c.) of 1M-hydrogen chloride in 4:1 ethanol-water, and hydrogen (3.60 c.c. at 20° and 750 mm.) was evolved. The molar ratio hydrogen:complex was 0.997:1. Another sample of the hydrido-complex (2.0 g.), suspended in ethanol (15 c.c.), was treated with the above hydrogen chloride solution (10 c.c.) under nitrogen. After the effervescence had ceased, the solvent was removed under reduced pressure and the residue was

recrystallised from benzene, yielding light yellow, diamagnetic crystals, m. p. 180—182°, soluble in polar organic solvents and in benzene (Found: C, 64.15; H, 5.3; Cl, 7.1. $C_{62}H_{49}Cl_3P_4Rh$ requires C, 64.3; H, 5.1; Cl, 7.3%); molar conductance ($10^{-3}M$ -solution in nitrobenzene at 25°), 17.8 ohm⁻¹.

Reaction of the Hydrido-complexes with Carbon Tetrachloride.—The hydrido-complexes of rhodium and of cobalt (0.1 g.) were treated with carbon tetrachloride (0.25 c.c.) under nitrogen. After a few minutes, the solvent was distilled off under reduced pressure, being collected in a solid carbon dioxide trap. Its infrared spectrum was recorded, using 0.1-mm. cells and carbon tetrachloride as reference. The presence of chloroform in the solvent was proved by the bands at 1217 and 668 cm.⁻¹.

Reaction of Di-(1,2-bisdiphenylphosphinoethane)rhodium(I) Chloride with Hydrogen Chloride.—A solution of $[Rh(DPE)_2]Cl$ (2.0 g.) in ethanol (20 c.c.) was treated as in (2) (see above) with a solution (10 c.c.) of 1M-hydrogen chloride in aqueous ethanol. Removal of the solvent under reduced pressure and recrystallisation of the residue from benzene gave a light yellow product, identified by means of its infrared spectrum, m. p., molar conductance in nitrobenzene solution (17.6 ohm⁻¹), diamagnetism, and analysis (Found: C, 62.3; H, 5.2; Cl, 7.0%) as the same compound as obtained in (2). On treatment with sodium tetraphenylborate in ethanolic solution, it gave a light yellow precipitate, m. p. 234°, slightly soluble in ethanol (Found: C, 72.5; H, 5.65; Cl, 2.75. $C_{76}H_{49}BClP_4Rh$ requires C, 72.6; H, 5.6; Cl, 2.8%).

Dihydridodi-(1,2-bisdiphenylphosphinoethane)cobalt(III) Perchlorate $[CoH_2(C_2H_4(PPh_2)_2)_2]ClO_4$.—A suspension of $[CoH(DPE)_2]$ (1.0 g.) in ethanol (30 c.c.) was treated with a solution (5 c.c.) of 1M-perchloric acid in 4:1 ethanol-water, and the mixture was stirred. The yellow crystals which slowly formed were filtered off, washed with ethanol, and dried. The complex is diamagnetic, slightly soluble in polar organic solvents, but insoluble in hydrocarbons, decomp. 185—186° (Found: C, 64.7; H, 5.3; Cl, 3.6. $C_{52}H_{50}ClCoO_4P_4$ requires C, 65.3; H, 5.3; Cl, 3.7%); molar conductance ($10^{-3}M$ -solution in nitrobenzene at 20°), 18.2 ohm⁻¹.

Dideuteridodi-(1,2-bisdiphenylphosphinoethane)cobalt(III) perchlorate was similarly prepared, in deuterated ethanol, from $[CoD(DPE)_2]$ and deuterated perchloric acid.

Reaction of the Hydrido-complex of Cobalt(III).— $[CoH_2(DPE)_2]ClO_4$ was treated with a solution of 1M-sodium hydroxide in 1:1 ethanol-water. The red substance formed after several hours was filtered off, washed with ethanol, dried, and identified as hydridodi-(1,2-bisdiphenylphosphinoethane)cobalt(I) by means of its infrared spectrum. The same reaction, carried out in aqueous 1M-sodium hydroxide, took about ten days for completion.

Dipole Moments.—These were determined as described previously,¹¹ and are listed in the Table.

	w_2	$\Delta\epsilon$	$\Delta\nu$	α_0	β	τ^P	ϵ^P	μ (D)	μ_{20} (D)
$[RhH(DPE)_2]$	0.01192	0.03305	-0.0049	2.77	-0.41	666.5	274	4.35	4.03
	0.01360	0.03688	-0.0056	2.71	-0.41	656.0	274		
$[CoH(DPE)_2]$	0.00832	0.01887	-0.0037	2.25	-0.45	539.3	274		
	0.00952	0.01954	-0.0044	2.05	-0.46	506.8	274	3.50	3.08

We thank Dr. Anna Segrè for the nuclear magnetic resonance spectra, and Dr. Angelo Mugnoli for the Debye spectra. This research was supported by the U.S. Air Force.

ISTITUTO DI CHIMICA GENERALE DELL'UNIVERSITÀ DI MILANO,
MILAN, ITALY.

[Received, July 29th, 1963.]

- ¹ Chatt, *Proc. Chem. Soc.*, 1962, 318.
- ² Vaska and DiLuzio, *J. Amer. Chem. Soc.*, 1961, **83**, 756; Malatesta, "Advances in the Chemistry of the Co-ordination Compounds," ed. Kirschner, Macmillan, New York, 1961, p. 475.
- ³ Lewis, Nyholm, and Reddy, *Chem. and Ind.*, 1960, 1386.
- ⁴ Zingales, Canziani, and Chiesa, *Inorg. Chem.*, 1963, **2**, 1303.
- ⁵ Chatt, Hart, and Rosevear, *J.*, 1961, 5504.
- ⁶ Vaska and DiLuzio, *J. Amer. Chem. Soc.*, 1961, **83**, 2784.
- ⁷ Vaska, *Symp. Inorg. Chem.*, June 1963, Cincinnati.
- ⁸ Chatt and Shaw, *J.*, 1962, 5075.
- ⁹ Edgell, Hagee, and Gallup, *J. Amer. Chem. Soc.*, 1956, **78**, 4185.
- ¹⁰ Chatt and Hart, *J.*, 1960, 1378.
- ¹¹ Sacco, *Gazzetta*, 1963, **93**, 542.