Journal of Organometallic Chemistry, 390 (1990) 97–104
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20769

Reductive carbonylation of cobalt(II) salts containing weakly-coordinating anions in the presence of diphosphine ligands

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(Received January 4th, 1990)

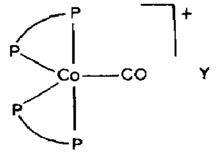
Abstract

The cobalt(I) carbonyl complexes $[Co(CO)(L-L)_2]Y$, $[Co_2(CO)_4(L-L)_3]Y_2$, and $[Co(CO)_3(L-L)]Y$ ($L-L$ = ditertiary phosphine; $Y = BF_4$, BPh_4) have been obtained by treating alcoholic solutions of cobalt(II) salts containing weakly-coordinating anions and diphosphines with carbon monoxide under ambient conditions. The types of products formed depend on the steric properties of the ligand L–L. The stereochemistry and dynamic behaviour of the products in solution have been studied by variable-temperature $^{31}P\{^1H\}$ NMR spectroscopy. A possible mechanism is suggested for the carbonylation reactions, which were found to involve formation of the diphosphine oxides.

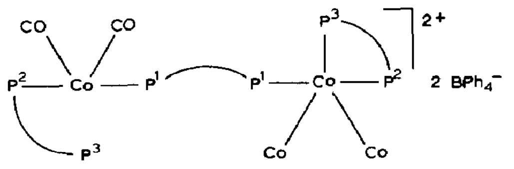
Introduction

The classical method for making of cobalt(I) cationic phosphinocarbonyl complexes involves disproportionation of dicobalt octacarbonyl in the presence of the appropriate phosphorus ligand [1]. With unidentate phosphines or phosphites (L) compounds of type $[Co(CO)_n(L)_{5-n}][Co(CO)_4]$ (n = 1, 2 or 3) have been obtained, the degree of substitution, n, varying with the size of ligand L [2]. Similarly, ditertiary phosphines (L–L) react with $[Co_2(CO)_8]$ to give, depending on the steric properties of the ligand, cobalt(I) complexes of type $[Co(CO)(L-L)_2]^+$, $[Co_2(CO)_4(L-L)_3]^{2+}$ or $[Co(CO)_3(L-L)]^+$, in which the anion $[Co(CO)_4]^-$ can be replaced by large, weakly-coordinating anions such as BPh_4^- [3]. Cationic carbonyl complexes can also be obtained by reduction [4], including sensitized-photoreduction [5], of cobalt(II) salts in the presence of CO and uni- or bi-dentate phosphines, or by addition or substitution reactions of phosphino- or phosphinocarbonyl-complexes of cobalt(I) [6].

Some years ago we showed [7] that cobalt(I) complexes of the type $[Co(CO)_n(L)_{5-n}]^+$ (L = secondary or tertiary phosphine) can be readily prepared under ambient conditions by reaction of carbon monoxide with alcoholic solutions



(1)



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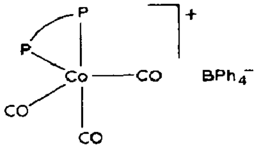
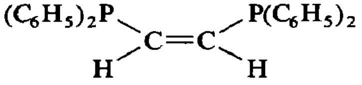


(3)

containing unidentate phosphines and a cobalt(II) salt with a weakly-coordinating anion. Under the same conditions carbon monoxide reacts with $[Co(H_2O)_6](BF_4)_2$ in the presence of the ligands $Ph_2PCH_2CH_2SR$ (P–S) (R = Me, Et or Ph) to give carbonyl complexes of the type $[Co(CO)_2(P\text{–}S)_2]^+$ [8]. In order to determine the limits of this synthetic route, we have now extended the study to a series of ditertiary phosphines:

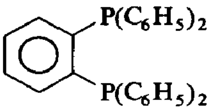
$(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2$

(n = 1, dppm; n = 2, dppe; n = 3, dppp)



$(C_6H_5)_2P(H)C{=}C(H)P(C_6H_5)_2$

(*cis*-dppv)



(*o*-pp)

$(C_2H_5)_2P(CH_2)_2P(C_2H_5)_2$

(depe)

$(C_6H_{11})_2P(CH_2)_2P(C_6H_{11})_2$

(dcpe)

We have thereby obtained diphosphinocarbonyl complexes of the types $[Co(CO)(L\text{–}L)_2]Y$ (**1**), **1a**: P–P = dppm, Y = BF_4; **1b**: P–P = depe, Y = BPh_4; **1c**: P–P = *o*-pp, Y = BF_4; **1d**: P–P = dppe, Y = BF_4; **1e**: P–P = *cis*-dppy, Y = BF_4) $[Co_2(CO)_4(L\text{–}L)_3](BPh_4)_2$ (**2**) (**2a**: P–P = dppp, **2b** P–P = dppe) and $[Co(CO)_3(L\text{–}L)]BPh_4$ (**3**) (**3a**: P–P = dppe).

In some cases formation of the cobalt(I) carbonyl complex requires the presence of a strong base (KOH) in the reaction mixture.

The carbonyl derivatives have been characterized by IR and $^{31}P\{^1H\}$ NMR spectroscopy. All the complexes are stereochemically non-rigid on the NMR time-scale, and for purposes of comparison we have also recorded low-temperature ^{31}P NMR data for some compounds previously prepared by other routes.

The study has provided another illustration of the ability of cobalt(II) salts and complexes to undergo reductive carbonylation under mild conditions [9].

Experimental

All operations were carried out under argon. Solvents were distilled, dried, and deoxygenated before use.

The diphosphine ligands were purchased from Strem Chemicals except for dcpe, which was made by a published method [10]. All other chemicals were purchased, and used without further purification. The complex $[Co_2(CO)_4(dppe)_3](BPh_4)_2$ was prepared by a published procedure [3b].

IR spectra were recorded on a Jasco DS 702 G spectrophotometer calibrated with polystyrene. $^{31}P\{^1H\}$ NMR spectra were recorded with a Bruker WP 80 SY Fourier transform spectrometer equipped with a variable-temperature probe; CH_2Cl_2 solutions were used. For temperatures lower than 183 K a CD_2Cl_2/CHF_2Cl (1/1) mixture was used as solvent. Positive chemical shifts are downfield from 85% H_3PO_4 as external standard.

Conductance data were obtained with a Metrohm Herisau E518 conductivity bridge. Melting points were determined with a Büchi 512 apparatus and are uncorrected. Elemental analyses were performed by the Microanalytical laboratory of our Institute.

Absorption of CO at constant pressure was monitored with a standard apparatus equipped with a thermostatted gas-burette.

Preparation of the complexes

Significant IR and ^{31}P NMR data for the compounds are listed in Table 1.

$[Co(CO)(dppm)_2]BF_4$ (1a), $[Co(CO)(depe)_2]BPh_4$ (1b), $[Co(CO)(o\text{-}pp)_2]BF_4$ (1c), $[Co_2(CO)_4(dppp)_3](BPh_4)_2$ (2a), and $[Co(CO)_3(dcpe)]BPh_4$ (3a). A dichloromethane solution (20 ml) of the appropriate ligand (2 mmol) was added to an ethanol solution (30 ml) of $[Co(H_2O)_6](BF_4)_2$ (1 mmol) under a CO atmosphere, and the mixture was stirred for two days. The complexes with dppm and *o*-pp were

Table 1

IR and $^{31}P\{^1H\}$ NMR data

Complex	IR [a] ν(CO) (cm^{-1})	^{31}P NMR [b,c]		
		δ (ppm)	J(P–P) (Hz)	T (K)
1a	1943	−6.8(s)		308
		−15.4(t),3.2(t)	98	133
1b	1916	68.9(s)		308
		61.9(t),81.1(t)	44	153
1c	1913	61.8(s)		308
		46.1(t),77.9(t)	38	183
1d	1919	68.6(s)		308
		63.6(t),83.5(t)	34	173
1e	1963	74.6(s)		308
		86.1(t),107.3(t)	42	133
2a	2002,1947	23.4(d),45.8(t)	29	308
		[d]		163
2b	2008,1956	51.4(t),70.3(d)	23	308
		[d]		163
3a	2071,2019,2003	105.5(s)		308
		108.3(s)		133

[a] Nujol mull. [b] ppm values relative to 85% H_3PO_4 external standard. Solvents: CH_2Cl_2 (308–183 K), CHF_2Cl/CD_2Cl_2 (183–133 K). [c] Abbreviations: s, singlet; d, doublet; t, triplet. [d] ABX spin systems. Lettering for P atoms as indicated in **2**. **2a**: δ_1 46.3, δ_2 6.5, δ_3 40.5 ppm, J_{12} 84, J_{13} 25, J_{23} 45 Hz. **2b**: δ_1 51.9, δ_2 87.5, δ_3 55.4 ppm, J_{12} 99, J_{13} 34, J_{23} 24 Hz.

obtained as BF_4 salts by removing the dichloromethane under reduced pressure. The more soluble compounds containing depe, dppp and dcpe were precipitated as tetraphenylborate salts by addition of a two-fold excess of $NaBPh_4$. Recrystallization from dichloromethane/2-propanol gave analytically pure compounds.

1b: Yellow. Anal. Found: C, 65.85; H, 8.33. $C_{45}H_{68}BCoOP_4$ calcd.: C, 66.02; H, 8.37%. Λ_M: 51 ohm^{-1} cm^2 mol^{-1}. M.p. (dec.): 142–144 °C. **2a**: Yellow. Anal. Found: C, 75.88; H, 5.64. $C_{133}H_{118}B_2Co_2O_4P_6$ calcd.: C, 75.86; H, 5.65%. Λ_M: 101 ohm^{-1} cm^2 mol^{-1}. M.p. (dec.): 117–119 °C. **3a**: Yellow-green. Anal. Found: C, 71.77; H, 7.70. $C_{53}H_{68}BCoO_3P_2$ calcd. C, 71.94; H, 7.75. Λ_M: 49 ohm^{-1} cm^2 mol^{-1}. M.p. (dec.): 143–145 °C.

$[Co(CO)(dppe)_2]BF_4$ (1d) and $[Co(CO)(cis\text{-}dppv)_2]BF_4$ (1e). A dichloromethane solution (20 ml) of the ligand (2 mmol) was added to an ethanol solution (30 ml) of $[Co(H_2O)_6](BF_4)_2$ (1 mmol) and KOH (1 mmol). The reaction vessel was then filled with CO, the solution stirred for 4 h, and its volume then halved under reduced pressure. Subsequent addition of 2-propanol (30 ml) gave a precipitate, which was recrystallized from dichloromethane/2-propanol.

Complexes **1a**, **1c**, **1d**, and **1e**, which have been reported previously, were identified from their elemental analyses and spectroscopic data.

Results and discussion

This study has shown that reductive carbonylation of cobalt(II) salts containing low-coordinating anions occurs under ambient conditions in the presence of diphosphine ligands. As found for the reaction with $[Co_2(CO)_8]$, the products are of the type $[Co(CO)(L-L)_2]Y$ (**1**), $[Co_2(CO)_4(L-L)_3]Y_2$ (**2**) or $[Co(CO)_3(L-L)]Y$ (**3**) (Y = BF_4, BPh_4), depending on the nature of the diphosphine. Thus when $[Co(H_2O)_6](BF_4)_2$ is stirred under carbon monoxide in dichloromethane/ethanol in the presence of an excess of dppm, depe, or *o*-pp the compounds $[Co(CO)(L-L)_2]Y$ (L–L = dppm, Y = BF_4 (**1a**); L–L = depe, Y = BPh_4 (**1b**); L–L = o-pp, Y = BF_4 (**1c**)) are obtained, whereas with the more hindered diphosphine dcpe the product is the tricarbonyl $[Co(CO)_3(dcpe)]BPh_4$ (**3a**). With the ligand dppp the major product is a binuclear cation of type **2**, which can be isolated as the solid salt $[Co_2(CO)_4(dppp)_3](BPh_4)_2$ (**2a**). The more soluble complexes **1b** and **3a** must also be precipitated as tetraphenylborate salts. No carbonylation is observed with the ligands dppe and *cis*-dppv under the same experimental conditions and the unreacted cobalt(II) complexes $[Co(L-L)_2](BF_4)_2$ are recovered from the reaction mixtures. However, the cobalt(I) monocarbonyls $[Co(CO)(L-L)_2]BF_4$ (L–L = dppe (**1d**); L–L = *cis*-dppv (**1e**)) are obtained in high yield when the reaction between $[Co(L-L)]_2(BF_4)_2$ and carbon monoxide is carried out in ethanol in the presence of free diphosphine and KOH (1/1/1 molar ratios).

All complexes, including the previously reported **1a** [6d], **1c** [5], **1d** [4a,4b,6b], and **1e** [6a], were characterized by elemental analysis, conductivity measurements, and IR and ^{31}P NMR spectroscopy.

Complexes **1a**–**1e** are diamagnetic, yellow to red solids and behave as 1/1 electrolytes in nitromethane. Their IR spectra show a strong $\nu(CO)$ band in the 1915–1965 cm^{-1} region, and a single resonance appears in the proton-decoupled ^{31}P NMR spectra. Since the $[Co(CO)(L-L)_2]^+$ cations are known to possess a trigonal-bipyramidal structure (TBP) [4b,5,6d], the ^{31}P NMR data clearly indicate that complexes (**1a**–**1e**) are stereochemically non-rigid on the NMR time-scale at room temperature. Fluxional behaviour for five-coordinate derivatives containing bidentate phosphines is commonly observed; for example for the $[M(CO)(L-L)_2]^+$ ($M = Rh$, Ir) complexes, which are known to have a TBP structure with an equatorial CO group [11]. When the temperature is lowered the single resonance broadens, and eventually splits into two triplets of equal intensity (Table 1), in agreement with a TBP structure, in which the diphosphine ligands span axial and equatorial positions. The low-field signal is assigned to the equatorial phosphorus atoms [12]; apparently the $J(P-P)$ values decrease with increase in the length of the phosphine backbone, as shown by the data for series **1a** > **1e** > **1c** > **1d** in the case of the phenyl-substituted ligands.

The IR spectrum of **2a** shows two CO stretching vibrations, at 2002 and 1947 cm^{-1}, consistent with a *cis* arrangement of the carbonyl groups. This complex behaves as a 1/2 electrolyte in nitromethane, and its dimeric nature in this solvent is confirmed by conductivity measurements at various concentrations (5×10^{-4}–10^{-2} mol dm^{-3}). The Onsager coefficient α, determined from the Onsager equation $\Lambda_0 = \Lambda_e + \alpha\sqrt{c_e}$ (Λ_0 and Λ_e = equivalent conductance at zero and c_e concentration, respectively), is 3.4 ohm^{-1} $dm^{7/2}$ $mol^{-3/2}$, in good agreement with values reported for 1/2 electrolytes [13]. Evidences for a binuclear structure of type **2** for **2a** also come from a ^{31}P NMR study. In dichloromethane solution at room temperature the ^{31}P NMR spectrum of the cation $[Co_2(CO)_4(dppe)_3]^{2+}$ shows a triplet and a doublet (1/2 intensity ratio) at 45.8 and 23.3 ppm, respectively. In agreement with the coordination chemical shift expected for diphosphine ligands involved six-membered rings [14], the high-field signal can be attributed to the atoms of a chelating diphosphine, with the low-field one assigned to the phosphorus atoms of a dppp molecule bridging two cobalt atoms. The two signals broaden as the temperature is lowered below −20 °C, the high-field one splitting into two broad signals. At −70 °C three well separated groups of lines are observed, and at −110 °C (CD_2Cl_2/CHF_2Cl solution) these separate into a spectrum consistent with an ABX spin system (see Fig. 1); in this case B and X are the phosphorous atoms of the chelating ligand. The analogous complex $[Co_2(CO)_4(dppe)_3](BPh_4)_2$ (**2b**), which can be prepared via disproportionation of $[Co_2(CO)_8]$ [3b], exhibits similar ^{31}P NMR behaviour. The room temperature spectrum again shows a doublet and a triplet at 70.3 and 51.4 ppm, in 2/1 intensity ratio, but with the resonance of the chelating dppe (five-membered ring) downfield from that of the bridging one. Complex **2b** is also stereochemically non-rigid at room temperature, and at −110 °C gives a limiting spectrum consistent with an ABX spin system (see Table 1). The magnitudes of the P–P coupling constants in complexes **2a** and **2b** are similar, except for the through-backbone constant which shows the expected dependence on the chelate ring size [15]. In similar phosphino cobalt(I) complexes, the $J(P-P)$ data have been used to distinguish between TBP and square pyramidal geometry [16], but in the case of **2a** and **2b** the values appear to be intermediate between those reported for the two different structures. However the OC–Co–CO angles, calculated on the basis of the relative intensities of the symmetric and antisymmetric CO stretching vibrations [17], are about 130° and 135° for **2a** and **2b**, respectively. We thus tentatively suggest for both complexes a distorted geometry of type **2**, which is more compatible with the calculated bond angles. An intramolecular exchange between axial and equatorial phosphorus atoms, which appears to be rapid at room temperature on the NMR time-scale, accounts for the temperature-dependence of ^{31}P NMR spectra of complexes **1** and **2**. The activation energy for this exchange process, judged from the temperature at which a static spectrum is obtained, appears to decrease with the bite of diphosphine ligand in the order dppp > dppe > dppm, as found for similar TBP diphosphino complexes [11,18].

The reductive carbonylation of $[Co(H_2O)_6](BF_4)_2$ in the presence of the diphosphine gives a type **3** tricarbonyl complex only in the case of the dcpe ligand. Complex **3a** is a yellow-green solid, which behaves as a 1/1 electrolyte in nitromethane. The IR spectrum in the 2075–2000 cm^{-1} region shows three stretching vibrations, as reported for the analogous complex containing the diarsine $Ph_2As(CH_2)_2AsPh_2$ [3b]. In dichloromethane solution **3a** is stereochemically non rigid on the NMR time scale, its NMR spectrum showing a single resonance even at −140 ° C, the lowest accessible temperature. The large coordination chemical shift (Δ 104.2 ppm) is in accord with the formation of a five-membered chelate ring [14], but the coordination geometry adopted by the metal atom is still not clear.

Quantitative aspects of the reductive carbonylation have been studied in the case of the $[Co(H_2O)_6](BF_4)$/*o*-pp system, which shows most favourable rate of CO uptake when 2-propanol was used as solvent because of its convenient vapour pressure. The volume of absorbed CO was measured at constant pressure in the presence of a fixed amount of cobalt(II) and at various *o*-pp/Co^{II} ratios (R). When a 2-propanol suspension of the cobalt(II) complex $[Co(o\text{-}pp)_2](BF_4)_2$ was stirred under a carbon monoxide atmosphere a slow, non-stoichiometric reduction to

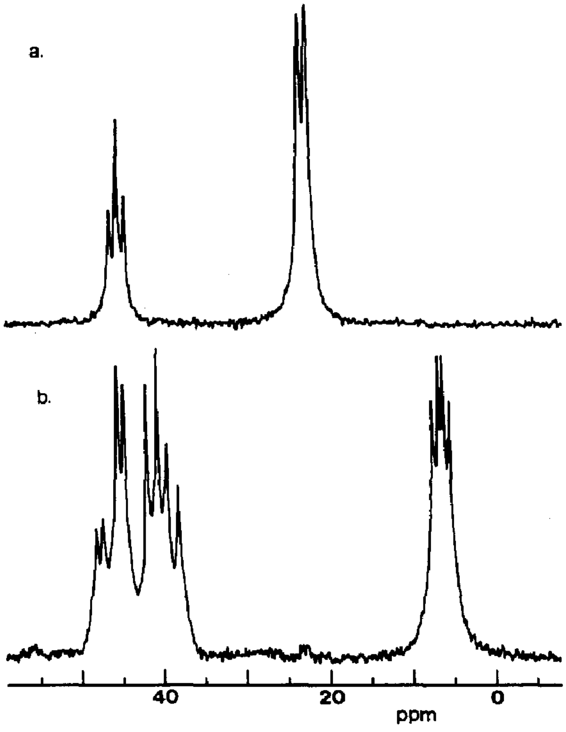


Fig. 1. $^{31}P\{^1h\}$ NMR spectra of $[Co_2(CO)_4(dppp)_3](BPh_4)_2$ (**2a**), (a) at 308 K (in CH_2Cl_2 solution), (b) at 163 K (in CD_2Cl_2/CHF_2Cl solution).

cobalt(I) carbonyl **1c** occurred. However, when the ligand *o*-pp was added under CO to a 2-propanol solution of $[Co(H_2O)_6](BF_4)_2$ in a molar ratio, $R > 2$, the gas absorption was faster, and the total uptake of carbon monoxide increased with increasing R. In the presence of an excess of *o*-pp ($R \geq 3$–3.5), one mole of CO per mole of cobalt(II) was absorbed, with quantitative formation of **1c**. Neither carbon dioxide nor acetone (from alcohol oxidation) was detected chromatographically in the reaction mixtures. The IR spectrum of the residue obtained by removal of the solvent showed the P=O bands typical of phosphine-oxide in the 1180–1200 cm^{-1} region. In addition, extraction with toluene gave solutions whose ^{31}P NMR spectra showed the presence of the diphosphine monoxide (*o*-ppO) (26.6, −15.4 ppm, J(P–P) 14.7 Hz), and of traces of diphosphine dioxide (29.5 ppm). The formation of phosphine oxides suggests that the reduction of cobalt(II) to cobalt(I) carbonyl derivatives takes place in accord with eq. 1, possibly with formation of the phosphonium salt of the diphosphine. In agreement with equation 1, a rapid and quantitative conversion of cobalt(II) was observed for $R = 2.5$ when the carbonylation was carried out in the presence of KOH (Co^{II}/KOH molar ratio 1/1).

$$2Co^{2+} + 5o\text{-pp} + H_2O + 2CO \rightarrow 2[Co(CO)(o\text{-pp})_2]^+ + o\text{-ppO} + 2H^+ \qquad (1)$$

The formation of diphosphine oxides was also detected by ^{31}P NMR in the reaction with dppm. The spectrum of the toluene extracts shows two doublets centred at 24.5 and −27.1 ppm (dppmO, J(P–P) 50.8 Hz), and a singlet at 23.7 ppm ($dppmO_2$). Analogously, when **1d** and **1e** are formed from $[Co(L–L)_2](BF_4)_2$/L–L/KOH (L–L = dppe and *cis*-dppv; 1/1/1 molar ratios), 1 mol of carbon monoxide per mol of cobalt is absorbed, with formation of the corresponding diphosphine monoxides, as shown by the ^{31}P NMR spectra of the toluene extracts (dppeO: 28.1, −12.9 ppm, J(P–P) 47.6 Hz; *cis*-dppvO: 17.0, −20.6 ppm, J(P–P) 4.9 Hz). It is concluded that the diphosphine is also the reducing agent in the presence of KOH.

The reductive carbonylation appears to proceed by one of two alternative paths. With the first group of bidentate ligands a Co^{II}–CO–diphosphine adduct is probably formed first, and is then reduced to the cobalt(I) carbonyl derivative by the diphosphine. The absence of reaction of the cobalt(II)-diphosphine systems with dppe and *cis*-dppv is apparently due to the inability of the complexes $[Co(L–L)_2]^{2+}$ to form an easily-reducible cobalt(II) carbonyl intermediate [8]. Addition of KOH provides an alternative path, which leads to carbonyl derivatives via the diphosphinocobalt(I) complexes $[Co(L–L)_2]BF_4$. Support for this hypothesis comes from experiments carried out under an inert atmosphere. When a suspension of the yellow complexes $[Co(L–L)_2](BF_4)_2$ in 2-propanol was shaken in the presence of diphosphine and KOH, there was ready transformation into the green cobalt(I) species $[Co(L–L)_2]BF_4$ in accord with reaction 2.

$$2[Co(L–L)_2](BF_4)_2 + L–L + 2KOH$$

$$\rightarrow 2[Co(L–L)_2]BF_4 + L–LO + H_2O + 2KBF_4 \qquad (2)$$

The reaction is similar to that involved in synthesis of zero-valent d^{10} phosphino metal complexes [19]. When reaction 2 is carried out under carbon monoxide, complexes of type **1** are formed through rapid coordination of CO to the unsaturated $[Co(L–L)_2]^+$ cation.

We conclude that the reductive carbonylation under mild conditions of cobalt(II) salts containing low-coordinating anions provides a simple and general method for the synthesis of cationic carbonyl complexes of cobalt(I) containing a variety of uni- and bi-dentate phosphines.

Acknowledgements

Support of this work by the Italian Consiglio Nazionale delle Ricerche, Rome, and by the Italian Ministero della Pubblica Istruzione is gratefully acknowledged. We thank Mr. F. Tubaro and Mr. P. Polese for technical assistance.

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