Cationic Carbonyls of Platinum, Palladium, and Nickel

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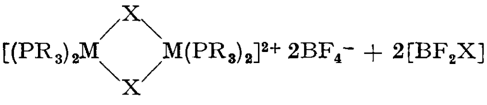
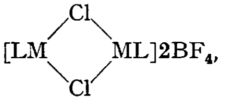
OUR recent characterization[1] of the platinum(II)-carbonyl cation, *trans*-$(PR_3)_2PtCl(CO)^+$ has led us to examine possible synthetic routes to analogous cations of the lighter transition metals, palladium, and nickel. While such ions are of interest in themselves they warrant special examination because of their isoelectronic relationship to Vaska's compound,[2] *trans*-$[IrCl(CO)(Ph_3P)_2]$, and the similar rhodium compound,[3] $[RhCl(Ph_3P)_3]$. We now describe a simple method of obtaining such cations, using dimeric, halogen-bridged cationic species related to those described recently[4] by Lappert *et al.* These have been prepared as the tetrafluoroborates by the reaction of the $(PR_3)_2$-MX_2 complexes with boron trifluoride in chloroform solution.

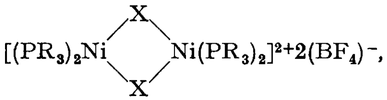
$$2(PR_3)_2MX_2 + 4BF_3 \rightarrow$$



$$[(PR_3)_2M(\mu\text{-}X)_2M(PR_3)_2]^{2+}\,2BF_4^- + 2[BF_2X]$$

These dimeric cations have been prepared for

$M = Pt$, $R = Et$ or Ph, and $X = Cl$, Br, or I, and for $M = Pd$, $R = Et$ or Ph and $X = Cl$. A similar complex  $[\mathrm{LM}\overset{\mathrm{Cl}}{\underset{\mathrm{Cl}}{\diamond}}\mathrm{ML}]2\mathrm{BF}_4$, where L = $Ph_2PCH_2{\cdot}CH_2{\cdot}PPh_2$, has also been prepared. With the two exceptions noted below, all of these complexes react extremely easily with carbon monoxide at atmospheric pressure with cleavage of the halogen-bridge (*cf.*, ref. 5) and formation of *trans*-$(PR_3)_2MX(CO)^+$ cations, isolated as BF_4^- salts. The ease of this cleavage for the platinum compounds is not markedly affected by the nature of the halogen or of the phosphine ligand, except that cleavage of the chelating phosphine complex does not occur even at 120° and 30 atm. CO pressure. Cleavage of the palladium complexes is ready for $R = Et$ but does not occur under mild conditions for $R = Ph$. The salt, $[(PEt_3)_2PdCl(CO)][BF_4]$ is sufficiently stable to allow full analytical and spectroscopic characterization, but after standing for 24 hr., considerable decomposition to the original chloride-bridged salt has occurred. This is one of the very few palladium carbonyl derivatives so far reported, others being largely confined to compounds[6-8] of the types $[Pd(CO)X_2]_n$, $Pd(CO)X_3^-$, and $[Pd_2(CO)_2Cl]_n$. The $(PEt_3)_2PdCl(CO)^+$ ion is characterized by the strong carbonyl absorption in the infrared spectrum at 2135 cm.$^{-1}$; its chemistry is currently being investigated.

We have, as yet, been unable to isolate the analogous dimeric, halogen-bridged nickel tetrafluoroborates,  $[(\mathrm{PR}_3)_2\mathrm{Ni}\overset{\mathrm{X}}{\underset{\mathrm{X}}{\diamond}}\mathrm{Ni}(\mathrm{PR}_3)_2]^{2+}2(\mathrm{BF}_4)^-$, but reactions of $(PR_3)_2NiX_2$ complexes with carbon monoxide and boron trifluoride in chloroform solution result in marked colour changes from red to yellow, and the formation of reaction mixtures which show for short periods of time strong infrared absorptions at *ca.* 2100 cm.$^{-1}$. It appears likely that $(PR_3)_2NiX(CO)^+$ ions may be produced, but that they are markedly less stable than their platinum and palladium analogues.

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[1] H. C. Clark, P. W. R. Corfield, K. R. Dixon, and J. A. Ibers, *J. Amer. Chem. Soc.*, 1967, **89**, 3360.
[2] L. Vaska and J. W. Di Luzio, *J. Amer. Chem. Soc.*, 1961, **83**, 2784.
[3] J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1966, 1711, and references therein.
[4] P. M. Druce, M. F. Lappert, and P. N. K. Riley, *Chem. Comm.*, 1967, 486.
[5] J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc.*, 1964, 1662.
[6] R. J. Irving and E. A. Magnusson, *J. Chem. Soc.*, 1958, 2283.
[7] J. S. Anderson, *Quart. Rev.*, 1947, **1**, 331.
[8] E. O. Fischer and A. Vogler, *J. Organometallic Chem.*, 1965, **3**, 161.