

Platinum Carbonyls Substituted by Tertiary Phosphines

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THIS work was undertaken in an attempt to produce well-defined carbonyl compounds of platinum(0) because the expected tetracarbonyl analogous to nickel tetracarbonyl is unknown,¹ and the reported compounds of the type $[\text{Pt}(\text{CO})_n(\text{PR}_3)_{4-n}]$ (R = hydrocarbon radicals) are unstable and difficult to obtain pure.² We now report the production of a series of surprisingly stable trinuclear platinum carbonyl derivatives and a less well-defined polymeric dicarbonyl $[\text{Pt}_n(\text{CO})_{2n}]$.

The dicarbonyl is obtained as a purple colloidal precipitate by the action of water on a benzene solution of $[\text{PtCl}_2(\text{CO})_2]$ under carbon monoxide. Deuterium oxide yields the same product, which probably has bridging and terminal carbonyl groups (i.r. spectrum: see Table). The action of

Tertiary phosphines react with the dicarbonyl suspended in acetone, to give poor yields of trinuclear carbonyl derivatives $[\text{Pt}_3(\text{CO})_3(\text{PET}_3)_4]$ and $[\text{Pt}_3(\text{CO})_3(\text{PPh}_3)_4]$ which are soluble in organic solvents.³ The latter is better obtained by the reaction of carbon monoxide with the phosphine, Na_2PtCl_4 , hydrazine, and potassium hydroxide in hot aqueous 90% ethanol. The exact details of the preparation are important, but using it, and other tertiary phosphines, carbonyl compounds of the six types listed in the Table were obtained. The known compounds (II), (III), and (IV) were obtained pure in beautiful crystals by this method, and we confirm that they dissociate in solution as previously reported.² The triphenylphosphine compounds are interconvertible and those of types E and F are most

TABLE

Types of tertiary phosphine derivatives of platinum carbonyls

	Compound	Type	m.p.*	Colour	$\nu(\text{CO}) \text{ cm.}^{-1}$ (i.r.)†
(I)	$[\text{Pt}_n(\text{CO})_{2n}]$	—	decomp.	see text	2068 s, 1891 s
(II)	$[\text{Pt}(\text{PPh}_3)_3]$	A	205—206°	golden yellow	—
(III)	$[\text{Pt}(\text{CO})(\text{PPh}_3)_3]$	B	decomp. $\sim 95^\ddagger$	pale yellow	1903 s
(IV)	$[\text{Pt}(\text{CO})_2(\text{PPh}_3)_2]$	C	decomp. $\sim 105^\ddagger$	white	1983 s, 1948 s
(V)	$[\text{Pt}(\text{CO})_2(\text{PPh}_2\text{Bz})_2]$	C	decomp. ~ 60	white	1985 s, 1940 s
(VI)	$[\text{Pt}_3(\text{CO})_3(\text{PPh}_2\text{Bz})_3]$	D	194—195	bright red	1784 s
(VII)	$[\text{Pt}_3(\text{CO})_3(\text{PPh}_3)_4]$	E	179—182§	bright red	1854 w, 1803 s, 1788 s
(VIII)	$[\text{Pt}_3(\text{CO})_4(\text{PPh}_3)_3]$	F	177—179§	black	1810 sh, 1797 s
(IX)	$[\text{Pt}(\text{CO})(\text{PMePh}_2)_3]$	B	108—110	white to cream	1908 s
(X)	$[\text{Pt}(\text{CO})_3(\text{PMePh}_2)_4]$	E	139—142§	red-violet	1847 w, 1796 s, 1769 s
(XI)	$[\text{Pt}_3(\text{CO})_4(\text{PMe}_2\text{Ph})_3]$	F	101—104§	brown	1800 s, 1779 s

* In evacuated tubes

† Nujol mull

‡ Turns yellow at $<100^\circ$, then melts at 185—190 (decomp.)

§ With decomposition

s = strong
sh = shoulder
w = weak

carbon monoxide on dilute ethanolic Na_2PtCl_4 gives a brown crystalline precipitate (with bands at 2062 and 1879 cm.^{-1}) of the same composition, which may be a purer form of the dicarbonyl. This substance is very sensitive to air and may even glow on exposure to it. The dicarbonyl is insoluble in all pure solvents but will dissolve in acetone to a green solution on addition of aqueous ammonia.

The ease of preparation falls as the phenyl groups are replaced by methyl, and all of the compounds, except (I) and type C, are stable in air in the solid state. Their carbon monoxide content was established by measuring the volume evolved on reaction with $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$, which yields $[\text{Pt}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$.⁴

The proton resonance spectra kindly measured by Dr. A. Pidcock, indicate three equivalent

¹ E. W. Abel, *Quart. Rev.*, 1963, **17**, 133.

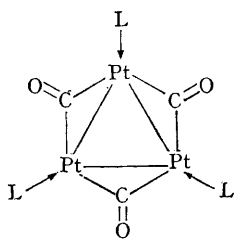
² L. Malatesta and C. Cariello, *J. Chem. Soc.*, 1958, 2323; L. Malatesta and R. Ugo, *J. Chem. Soc.*, 1963, 2080; F. Cariati, R. Ugo, and F. Bonati, *Chem. and Ind.*, 1964, 1714.

³ Originally mentioned as $[\text{Pt}_3(\text{CO})_4(\text{PR}_3)_4]$, see G. Booth, *Adv. Inorg. Radiochem.*, 1964, **6**, 47.

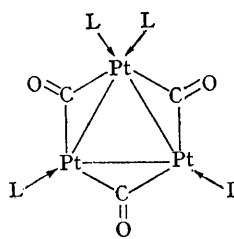
⁴ J. Chatt and G. A. Rowe, *Nature*, 1961, **191**, 1191.

benzyl groups in (VI) and two different types of methyl groups in the ratio 1:1 in (X). The infrared spectra suggest that all the carbonyl groups are bridging in compounds of types D, E,

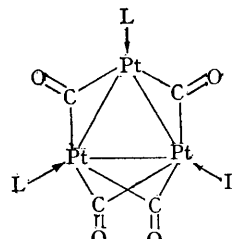
shows that the nickel-Group metal carbonyls are more closely related to those of the iron Group than had previously been realised.⁵ Third, the platinum triangle provides only the second example



Type D



Type E



Type F

and F. We therefore propose the following structures for the trinuclear derivatives. The dicarbonyl (I) may have a D-type structure (L = CO) or an analogous infinite linear structure.

Triangles of transition-metal atoms are becoming a common feature of transition-metal chemistry, but our series is interesting on three counts. First, it is the only one of platinum. Second, it

of such a metal cluster, after the $[\text{Re}_3\text{X}_{9+n}]^{n-}$ (X = Cl or Br; $n = 1-3$) series of ions, which shows a variable co-ordination number.⁶ It promises to show even greater variation, depending on the ligand L, and this aspect is now undergoing investigation.

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⁵ See $[\text{Os}_3(\text{CO})_{12}]$, E. R. Corey and L. F. Dahl, *Inorg. Chem.*, 1962, 1, 521.

⁶ J. E. Fergusson and B. H. Robinson, *Proc. Chem. Soc.*, 1964, 189, and references therein.