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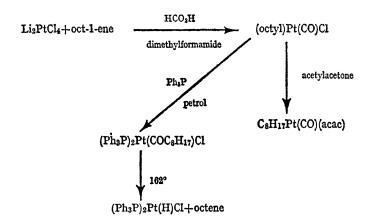
Alkylplatinum Carbonyl Chlorides

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A SIMPLE preparation of a novel class of transition-metal alkyl derivatives is reported. Lithium tetrachloroplatinate(II) dissolved in dimethylformamide is warmed with a mixture of oct-1-ene and formic acid and the resulting octylplatinum derivative can be extracted with isopentane in yields of 20—40%. The constitution of the

absorption at 720 cm. $^{-1}$ indicated the presence of a long-chain alkyl group. The material yielded a crystalline acetylacetonate, $C_8H_{17}Pt(CO),C_5H_7O_2$ in which the platinum–carbonyl and platinum–alkyl groups were retained. Proton magnetic resonance determinations on the acetylacetonate demonstrated the presence of one octyl group per



product, an oil, was established as follows. In the infrared spectrum, no trace of unsaturation was detectable in the region 1500—1600 cm. $^{-1}$ but intense absorption occurred at 2060 cm. $^{-1}$ (ν_{co}) and

acetylacetonate group and also the primary nature of the octyl group. The original chloro-compound was thus chloro(octyl)carbonylplatinum(II).

When the chloro-compound was added to a

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solution of triphenylphosphine in petrol a solid precipitated (m.p. 156°) which showed no absorption at 2060 cm.-1 but had a moderate absorption peak at 1639 cm.-1 which is characteristic of a platinum-acyl group.1 The compound was thus chloro(nonanoyl)bis(triphenylphosphine)platinum(II). Thermal decomposition of this compound at 162° in vacuo gave a product which, when recrystallised, afforded white crystals m.p. 215-220° This substance showed absorptions at 2231 cm.-1 (ν_{Pt-H}) and 832 cm.-1 (δ_{Pt-H}) and established the compound to be hydrochlorobis(triphenylphosphine)platinum(II).2 Oct-1-ene was also formed in the decomposition reaction and this is taken as evidence for the presence of the original eight-carbon fragment as a saturated alkyl group since the following interconversions are already known1,2:

Ethyl-, propyl-, and heptyl-platinum carbonyl chlorides were also made by the above method, pressures up to 50 atmospheres being used in the case of the lower alkyls. The ethyl compound had m.p. 65° and the presence of an ethyl group was clearly shown by proton magnetic resonance determinations. These compounds, which probably exist as dimers, are only moderately stable even when kept at 0°c but there seems little difference in stability between the ethyl and octyl derivative. Although Chatt and Shaw³ have prepared Pt(Buⁿ)₂(PMe₃)₂ and Pt(C₆H₅CH₂)Cl(PEt₃)₂ other authors4 have found a decline in stability of alkyl-transition-metal bonds with increase in size of the alkyl group and the present series of compounds seems to be the first in which the higher members have been obtained.

$$C_nH_{2n+1}CO \text{ PtX}(PR_3)_2 \xrightarrow{\text{heat}} C_nH_{2n+1} \text{ PtX}(PR_3)_2 \xrightarrow{\text{heat}} \text{ HPtX}(PR_3)_2$$

$$(X = \text{halogen, } R = \text{alkyl})$$

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⁴C. R. Kistner, J. H. Hutchinson, J. R. Doyle, and J. C. Storlie, Inorg. Chem., 1963, 2, 1255.