Internal Metallation of Tertiary and Secondary Carbon Atoms

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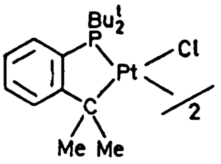
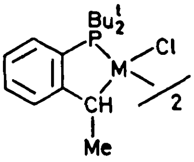
Summary The first example of a compound containing a tertiary carbon atom bonded to a transition metal has been prepared by platination of $PBu^t_2(o\text{-}Pr^iPh)$: some metallations of the secondary carbon atom of an *ortho*-ethylphenyl group, are also described.

There is growing interest in the intramolecular metallation of nitrogen- or phosphorus-donor ligands by transition metals.[1] Hitherto most metallations have been of aryl carbon atoms, although there are a number of metallations of methyl groups bonded to an aromatic ring.[2] Ethyl[3] and an n-propyl[2] groups have also been metallated although it is not known whether the β-(*i.e.* secondary) or the γ-(*i.e.* primary) carbon atom of the n-propyl group is the one attacked. One would anticipate, by analogy with alkyl derivatives of the sub-Group B metals, that the ease of metallation of carbon atoms would decrease in the order primary > secondary > tertiary. We have shown previously that bulky substituents on a tertiary phosphine ligand promote the tendency to metallate aryl or benzylic carbon atoms and we now find that they will promote metallation of secondary and even tertiary carbon atoms. Thus when dichlorobis(benzonitrile)platinum is heated in n-propanol with $PBu^t_2(o\text{-}Pr^iPh)$ for 4 h $[PtClPBu^t_2(CMe_2\text{-}C_6H_4)]_2$ (I) is formed in 65% yield. This is the first example of a compound containing a transition metal bonded to a tertiary carbon atom. The complex undergoes bridge splitting reactions with ligands such as pyridine, triphenylphosphine or dimethylphenylarsine (L) to give mononuclear species $[PtCl(PBu^t_2C_9H_{10})L]$ (with L *trans* to P). One might expect the tertiary carbon in (I) to be susceptible to electrophilic attack. However, the complex was recovered unchanged after treatment with dry hydrogen chloride in dry chloroform for several days at 20°.

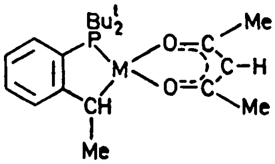
We also find that the ethyl group of $PBu^t_2(o\text{-}EtPh)$ is readily metallated, at the secondary carbon atom. Thus with $[PtCl_2(PhCN)_2]$ the complex $[MCl(PBu^t_2C_8H_8)]_2$ (II) (M=Pt) is formed. With sodium chloropalladite the complex $[PdCl_2(PBu^t_2C_8H_9)_2]$ is first produced but this on heating gives the binuclear internally metallated complex (II) (M=Pd). These platinum- or palladium-complexes (II) undergo bridge splitting reactions with ligands such as



(I)



(II)



(III)

triphenylphosphine, pyridine *etc.* and also give mononuclear acetylacetonates (III) when treated with thallium acetylacetonate. The ethyl group of PPh_2(*o*-EtPh) can be metallated by platinum but much more slowly than with PBu^t_2(*o*-EtPh).

All these complexes have been characterized by microanalysis, i.r. and ^1H n.m.r. spectroscopy and, in some cases, by ^{31}P- and ^{13}C-n.m.r. spectroscopy. In the ^1H n.m.r. spectrum of (III) (M=Pt) double resonance shows that $^2J(\text{Pt-C}H)$(121·6 Hz) and $^3J(\text{PtCH-CH}_3)$(42·1 Hz) are opposite in sign.

We thank Johnson Matthey Ltd. and the Science Research Council for generous support and Dr. B. E. Mann for some of the n.m.r. measurements.

(*Received, November* 15*th*, 1971; *Com.* 1966.)

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