Carboxylato(triphenylphosphine) Complexes of the Platinum Metals

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Summary The reactions of hydrido- and low oxidation state-triphenylphosphine derivatives of the platinum metals with carboxylic acids are shown to afford a convenient general route to complexes containing monodentate or bidentate carboxylate ligands.

Although tertiary phosphine–carboxylate derivatives of the platinum group metals feature extensively in homogeneous catalysis,[1] no systematic study of their synthesis has been reported. We now find that many hydrido- and low oxidation state-triphenylphosphine complexes of the platinum metals† react with a wide variety of carboxylic acids (RCOOH; R = alkyl, aryl, CF_3) to yield carboxylate derivatives. This previously known but hitherto neglected technique affords a convenient general route to a range of carboxylate derivatives including several species of signifi-

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† We have recently described simple, single stage syntheses for the precursors used in the present syntheses.[5]

cance as catalysts. Thus Wilkinson's selective hydrogenation catalysts,[1a] $RuH(OCOR)(PPh_3)_3$, and their hitherto unknown osmium analogues, $OsH(OCOR)(PPh_3)_3$, are rapidly precipitated as moderately air-stable crystalline solids on treating $RuH_2(PPh_3)_4$ and $OsH_4(PPh_3)_3$ respectively with carboxylic acids in boiling 2-methoxyethanol. These ruthenium and osmium carboxylates have similar spectroscopic properties; moreover *X*-ray powder photographs suggest that the acetate derivatives $MH(OCOMe)(PPh_3)_3$ are isostructural. The ruthenium complexes, $RuH(OCOR)(PPh_3)_3$, may also be obtained directly as crystalline precipitates by successive addition of ruthenium trichloride, carboxylic acid, and potassium hydroxide to triphenylphosphine in boiling ethanol. Other ruthenium carboxylates synthesised by the general route outlined above include the new series of complexes, $RuH(OCOR)(CO)(PPh_3)_2$, $RuCl(OCOR)(CO)(PPh_3)_2$, and $Ru(OCOCF_3)_2(CO)(PPh_3)_2$ [obtained from the hydrides $RuH_2(CO)(PPh_3)_3$ and $RuHCl(CO)(PPh_3)_3$], and $Ru(OCOCF_3)_3(NO)(PPh_3)_2$ [prepared from $Ru(NO)_2(PPh_3)_2$].

The osmium carbonyl hydrides, $OsHCl(CO)(PPh_3)_3$, $OsH_2(CO)(PPh_3)_3$, and $OsH_2(CO)_2(PPh_3)_2$, though resistant to weaker carboxylic acids, react with trifluoroacetic acid in benzene to yield derivatives which include $OsCl(OCOCF_3)(CO)(PPh_3)_3$, $Os(OCOCF_3)_2(CO)(PPh_3)_2$, and $Os(OCOCF_3)_2(CO)_2(PPh_3)_2$. These and other trifluoroacetates undergo metathetical exchange with sodium carboxylates in boiling acetone. I.r. spectra of the ruthenium and osmium diacetates $M(OCOMe)_2(CO)(PPh_3)_2$ confirm the presence of monodentate and bidentate acetate ligands in each complex. However the acetate ligands present in these complexes give rise to a single sharp peak in their ^1H n.m.r. spectra at 323 K; on cooling each specimen to 213 K this peak broadens then splits into two sharp lines of equal intensity. This behaviour, which is being further investigated, appears to be indicative of a novel, labile monodentate–bidentate acetate exchange process.

The new rhodium carboxylates $Rh(NO)(OCOR)_2(PPh_3)_2$, $Rh(OCOR)(CO)(PPh_3)_2$,‡ and $Rh(OCOR)(PPh_3)_3$‡ are readily obtained from $Rh(NO)(PPh_3)_3$, $RhH(CO)(PPh_3)_3$, and $RhH(PPh_3)_4$ respectively on treatment with carboxylic acids. The iridium(I) complex, $IrH(CO)(PPh_3)_3$ undergoes a series of oxidative–addition and reductive–elimination reactions with carboxylic acids; thus with excess of trifluoroacetic acid the reaction sequence (1) has been established by high-field

$$\begin{aligned} &IrH(CO)(PPh_3)_3 \longrightarrow [IrH_2(CO)(PPh_3)_3]^+ \\ &\longrightarrow IrH_2(OCOCF_3)(CO)(PPh_3)_2 \\ &\qquad \longrightarrow IrH(OCOCF_3)_2(CO)(PPh_3)_2 \end{aligned} \tag{1}$$

n.m.r. spectroscopy and by isolation of products. Similar reaction sequences are observed with other carboxylic acids. These results confirm and extend independent investigations reported while this work was in progress.[2,3]

The platinum hydride, $PtHCl(PPh_3)_2$ is resistant to weaker carboxylic acids but reacts with trifluoroacetic acid in benzene to afford the known[4] hydride complex $PtH(OCOCF_3)(PPh_3)_2$ as the major product.

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‡ The synthesis of these complexes by other more circuitous routes was reported while this work was in progress.[1c,6]

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