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Tricyclohexylphosphine Complexes of Rhodium, Iridium and Ruthenium

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Our interest in activation of carbon dioxide [1] and the report of a well-characterized $Ni(CO_2)(PCy_3)_2$ complex (PCy_3 = tricyclohexylphosphine) [2] led us to investigate tricyclohexylphosphine complexes of rhodium, iridium, and ruthenium. The basic and bulky phosphine is a good ancillary ligand for a coordinatively unsaturated complex likely to react with small gas molecules; this had been well-documented for rhodium [3], but at the time our studies were initiated little had been reported on iridium and ruthenium species, although carbonyls complexes such as $IrCl(CO)(PCy_3)_2$ [4], $HRuCl(CO)(PCy_3)_2$ [5], $RuCl_2(CO)(PCy_3)_2$ [5] and $Ru(CO)_3(PCy_3)_2$ [6] were known.

Other relevant papers on rhodium and iridium systems have appeared more recently [7–9]; one of these [9], reporting partial dehydrogenation of the tricyclohexylphosphine by Rh(I) and Ir(I), overlapped with some of our studies which were reported almost simultaneously at a conference [10].

The paper here summarizes our findings on some rhodium, iridium and ruthenium systems.

Use of single-stage syntheses [11], involving rapid mixing of alcoholic solutions of commercially available platinum metal halides with PCy_3, sometimes in the presence of borohydride [12], gives high yields of $HRuCl(CO)(PCy_3)_2$ [5], $Ru(CO)_3(PCy_3)_2$ [6], $RhCl(CO)(PCy_3)_2$ [4], $HRhCl_2(PCy_3)_2$ [7], and $IrCl(CO)(PCy_3)_2$ [4]. The procedures are simpler and quicker than the literature methods noted: thus, the carbonyl syntheses do not require the use of gaseous carbon monoxide, and the hydride syntheses involve no HCl solutions. For example, $RhCl(CO)(PCy_3)_2$ is readily obtained on rapidly mixing hot ethanolic solutions of $RhCl_3 \cdot 3H_2O$, KOH and the phosphine; the same carbonyl is formed on mixing the cycloocta-1,5-diene-(COD) dimer $[RhCl(COD)]_2$ [13] with the phosphine in CH_2Cl_2/CH_3OH, even at 20 °C. Abstraction of CO from alcohols is much more pronounced with the more basic tricyclohexylphosphine (compared, for example, to triphenylphosphine). Addition of the phosphine to $[RhCl(COD)]_2$ in CH_2Cl_2 alone leads to $RhCl(COD)(PCy_3)$ as reported recently by another group [14]. The iridium analogue, $IrCl(COD)(PCy_3)$, may be formed by addition of the phosphine to the easily made and handled $[HIrCl_2(COD)]_2$ complex [15]; the phosphine is sufficiently basic to remove HCl and this circumvents the necessity of isolating the somewhat more elusive $[IrCl(COD)]_2$ complex [8].

Treatment of the cyclooctene (COT) complex $[IrCl(COT)_2]_2$ [16] with PCy_3 in toluene at 20 °C under argon yields $H_2\overline{IrCl[P(C}_6H_9)Cy_2](PCy_3)$, *1*, in which one cyclohexyl group has been dehydrogenated to a cyclohexene group, the double bond of which is coordinated to the iridium. This interesting reaction was discovered independently and recently reported on by Vrieze *et al.* [9]. However, they had used refluxing conditions and this led to the 4-coordinate iridium(I) species $\overline{IrCl[P(C}_6H_9)Cy_2](PCy_3)$. The *cis*-dihydride was then isolated as a mixture of isomers only after further reaction with H_2; our spectroscopic data [ν(M–Cl), ν(Ir–H), $\delta\ ^{31}P$, J(P–P)] are in excellent agreement with theirs, and we have also found τ values (C_6D_6) at 19.8, 31.4 for the dominant isomer (~ 80% of the total via our method) which is one of two possible species containing a 5.5-membered ring [9]. The coordinated olefinic bond in complex *1* is not hydrogenated using 1 atm H_2, although such stoichiometric hydrogenation is well-documented for unstaruated phosphines such as *o*-vinylphenyldiphenylphosphine when coordinated at rhodium [17]. The 'saturated' dihydride $H_2IrCl(PCy_3)_2$ is readily synthesized by treating $[IrCl(COT)_2]_2/PCy_3$ solutions with 1 atm H_2, as reported by Vrieze *et al.* [9]. We have monitored dihydride formation at 20 °C by following an irreversible absorption of 1.0 mol H_2/Ir, and thus the noted [9] hydrogenation of the cyclooctene likely takes place subsequently. Use of D_2 gives a dideuteride [ν(Ir–D) 1605 cm^{-1}] but also some dihydride and a deuteride hydride, suggesting that there is some concomitant hydrogen exchange with the phosphine ligand. Treatment of the dihydride with deuterium leads to a dideuteride (and *vice versa*) and, since dihydride formation is essentially irreversible under the same conditions, these data again indicate some exchange process with the phosphine; nevertheless, the ^{31}P NMR of $H_2IrCl(PCy_3)_2$ remains as a singlet [9] even at −85 °C showing complete equivalence of the phosphine ligands. The analogous rhodium complex $H_2RhCl(PCy_3)_2$ [9] undergoes similar exchange with D_2.

Reaction of $H_2IrCl(PCy_3)_2$ with 1 atm CO gives a new species $H_2IrCl(CO)(PCy_3)_2$ (Table I), which shows no exchange with D_2 presumably because

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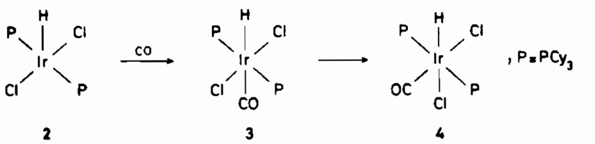
TABLE I. Some Spectroscopic Data[a] for Rhodium and Iridium Cyclohexylphosphine Complexes.

Complex	ν(CO)	ν(M–H)	ν(M–Cl)	τ(M–H)	$\delta^{31}P$
$H_2IrCl(CO)(PCy_3)_2$	1970	2200 2102	255	18.4(d of t)[b] 30.1(d of t)[b]	–24.2(s)
$HIrCl_2(PCy_3)_2$	–	c	317	42.3(t)[d]	–20.9(s)
$HIrCl_2(PCy_3)_2(DMA)$	1628	2300	300	–	–
3, $HIrCl_2(CO)(PCy_3)_2$	1980	2105	310	18.2(t)[e]	–2.3(s)
$HRhCl_2(PCy_3)_2$	–	1943	345	40.5(d of t)[f]	–

[a] ν in cm^{-1} (Nujol). NMR in $CDCl_3$ or C_6D_6; ^1H relative to TMS; ^{31}P relative to 85% H_3PO_4, downfield shifts being negative; s = singlet, d = doublet, t = triplet. [b] $J(H_A–H_B)$ = 5 Hz, $J(P–H_A)$ = 13 Hz, $J(P–H_B)$ = 18 Hz. [c] Not observed. [d] J(P–H) = 11 Hz. [e] J(P–H) = 11 Hz. [f] J(P–H) = 12 Hz, J(Rh–H) = 30 Hz.

this complex, unlike $H_2IrCl(PCy_3)_2$, is coordinatively saturated and cannot accommodate the necessary C–H cleavage (oxidative addition) [5, 18].

The monohydride $HIrCl_2(PCy_3)_2$ (Table I) is precipitated as a rose-coloured solid on adding $IrCl_4$ (Platinum Chemicals) in 2-methoxyethanol to a stirred, boiling solution of the phosphine in the same solvent; this hydride was probably synthesized previously but incorrectly formulated as $IrCl_2(PCy_3)_2$ [4]. The hydride is also formed via addition of HCl to solutions of $[IrCl(COT)]_2$ and PCy_3 in toluene, or toluene/NN-dimethylacetamide (DMA); with the latter solvent system, the hydride (Table I) precipitates as a yellow microcrystalline compound containing weakly coordinated amide that readily dissociates on dissolution in toluene. The ν(Ir–H) stretch, although not detectable in the 5-coordinate complex (and this is common for such species [19]) is readily detected in the DMA complex at 2300 cm^{-1}, an extremely high wavenumber for a metal–hydride stretch [20], presumably reflecting the weak binding of the *trans* amide ligand. Structure *2* for the 5-coordinate complex is consistent with the spectroscopic data, and reaction with 1 atm CO gives the carbonyl $HIrCl_2(CO)(PCy_3)_2$, *3* (Table I); the equivalence of the phosphines is shown by the ^{31}P and the high-field ^1H NMR, and the low τ value is consistent with hydride being *trans* to CO rather than Cl. Complex *3*, even in the solid state, isomerizes to *4*, and also eliminates HCl to yield *trans*-$IrCl(CO)(PCy_3)_2$. Complex *4* has been characterized previously [ν(CO) = 2015, ν(IrH) = 2276 cm^{-1}], having been made by reaction of $IrCl(CO)(PCy_3)_2$ with HCl [4].



2 3 4

The $[RhCl(COT)_2]_2/PCy_3$ systems were also studied by Vrieze *et al.* [9] and they noted formation of $RhCl[P(C_6H_9)Cy_2](PCy_3)$ and $H_2RhCl(PCy_3)_2$, analogous to the iridium species. However, we find that treatment of $[RhCl(COT)_2]_2$ with PCy_3 in toluene at 20 °C also yields $HRhCl_2(PCy_3)_2$ (Table I), which is more readily synthesized by treatment of $RhCl_3 \cdot 3H_2O$ with PCy_3 in acetone; this hydride has been made previously by reaction of HCl with $RhCl(PCy_3)_2$, but the high-field ^1H NMR had not been detected [7].

Table I lists spectroscopic data for the new complexes, and further data for the $HRhCl_2(PCy_3)_2$ complex.

Toluene solutions of the $[MCl(COT)_2]_2$ complexes (M = Rh, Ir) in the presence of PCy_3 at 25 °C were found to *sometimes* [21] absorb 1.0 mol CO_2 per metal atom, but we have not been able to isolate any CO_2 complexes. In view of the reactions noted above in the absence of CO_2 (for example, hydride formation), the CO_2 reactions are likely to be complex. Solution IR shows the presence of carbonyls (possibly $M(PCy_3) + CO_2 \rightarrow M(CO) + OPCy_3$, [22]) although a band at 1755 cm^{-1} in the iridium system could be due to ν(C=O) of coordinated CO_2 [23]. Carbon dioxide complexes of rhodium(I) have been synthesized by a similar procedure but using PBu^n_3 as the bulky phosphine [22]; few details were reported, but we found no evidence [24] for any reaction of $[RhCl(olefin)_2]_2/PBu^n_3$ solutions with 1 atm CO_2 at 20 °C (olefin = COT, C_2H_4).

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