

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 $\text{Ni}(\text{CO})_2(\text{PCy}_3)_2$ 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 carbonyl complexes such as $\text{IrCl}(\text{CO})(\text{PCy}_3)_2$ [4], $\text{HRuCl}(\text{CO})(\text{PCy}_3)_2$ [5], $\text{RuCl}_2(\text{CO})(\text{PCy}_3)_2$ [5] and $\text{Ru}(\text{CO})_3(\text{PCy}_3)_2$ [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 $\text{Rh}(\text{I})$ and $\text{Ir}(\text{I})$, 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 $\text{HRuCl}(\text{CO})(\text{PCy}_3)_2$ [5], $\text{Ru}(\text{CO})_3(\text{PCy}_3)_2$ [6], $\text{RhCl}(\text{CO})(\text{PCy}_3)_2$ [4], $\text{HRhCl}_2(\text{PCy}_3)_2$ [7], and $\text{IrCl}(\text{CO})(\text{PCy}_3)_2$ [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, $\text{RhCl}(\text{CO})(\text{PCy}_3)_2$ is readily obtained on rapidly mixing hot ethanolic solutions of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, KOH and the phosphine; the same carbonyl is formed on mixing the cycloocta-1,5-diene-(COD) dimer $[\text{RhCl}(\text{COD})]_2$ [13] with the phosphine in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$, 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 $[\text{RhCl}(\text{COD})]_2$ in CH_2Cl_2 alone leads to $\text{RhCl}(\text{COD})(\text{PCy}_3)$ as reported recently by another group [14]. The iridium analogue, $\text{IrCl}(\text{COD})(\text{PCy}_3)$, may be formed by addition of the phosphine to the easily made and handled $[\text{HirCl}_2(\text{COD})]_2$ complex [15]; the phosphine is sufficiently basic to remove HCl and this circumvents the necessity of isolating the somewhat more elusive $[\text{IrCl}(\text{COD})]_2$ complex [8].

Treatment of the cyclooctene (COT) complex $[\text{IrCl}(\text{COT})_2]_2$ [16] with PCy_3 in toluene at 20°C under argon yields $\text{H}_2\text{IrCl}[\text{P}(\text{C}_6\text{H}_9)\text{Cy}_2](\text{PCy}_3)$, **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 $\text{IrCl}[\text{P}(\text{C}_6\text{H}_9)\text{Cy}_2](\text{PCy}_3)$. The *cis*-dihydride was then isolated as a mixture of isomers only after further reaction with H_2 ; our spectroscopic data [$\nu(\text{M}-\text{Cl})$, $\nu(\text{Ir}-\text{H})$, $\delta^{31}\text{P}$, $J(\text{P}-\text{P})$] 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 ($\sim 80\%$ 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 unstaturated phosphines such as *o*-vinylphenyldiphenylphosphine when coordinated at rhodium [17]. The 'saturated' dihydride $\text{H}_2\text{IrCl}(\text{PCy}_3)_2$ is readily synthesized by treating $[\text{IrCl}(\text{COT})_2]_2/\text{PCy}_3$ 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 [$\nu(\text{Ir}-\text{D})$ 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 $\text{H}_2\text{IrCl}(\text{PCy}_3)_2$ remains as a singlet [9] even at -85°C showing complete equivalence of the phosphine ligands. The analogous rhodium complex $\text{H}_2\text{RhCl}(\text{PCy}_3)_2$ [9] undergoes similar exchange with D_2 .

Reaction of $\text{H}_2\text{IrCl}(\text{PCy}_3)_2$ with 1 atm CO gives a new species $\text{H}_2\text{IrCl}(\text{CO})(\text{PCy}_3)_2$ (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	$\nu(\text{CO})$	$\nu(\text{M-H})$	$\nu(\text{M-Cl})$	$\tau(\text{M-H})$	$\delta^{31}\text{P}$
$\text{H}_2\text{IrCl}(\text{CO})(\text{PCy}_3)_2$	1970	2200 2102	255	18.4(d of t) ^b 30.1(d of t) ^b	-24.2(s)
$\text{HIrCl}_2(\text{PCy}_3)_2$	—	c	317	42.3(t) ^d	-20.9(s)
$\text{HIrCl}_2(\text{PCy}_3)_2(\text{DMA})$	1628	2300	300	—	—
3, $\text{HIrCl}_2(\text{CO})(\text{PCy}_3)_2$	1980	2105	310	18.2(t) ^e	-2.3(s)
$\text{HRhCl}_2(\text{PCy}_3)_2$	—	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 $J(\text{H}_\text{A}-\text{H}_\text{B}) = 5 \text{ Hz}$, $J(\text{P}-\text{H}_\text{A}) = 13 \text{ Hz}$, $J(\text{P}-\text{H}_\text{B}) = 18 \text{ Hz}$.

^cNot observed.

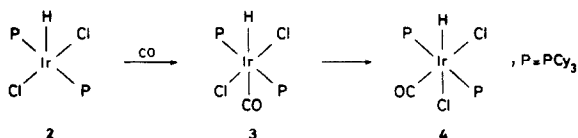
^d $J(\text{P}-\text{H}) = 11 \text{ Hz}$.

^e $J(\text{P}-\text{H}) = 11 \text{ Hz}$.

^f $J(\text{P}-\text{H}) = 12 \text{ Hz}$, $J(\text{Rh}-\text{H}) = 30 \text{ Hz}$.

this complex, unlike $\text{H}_2\text{IrCl}(\text{PCy}_3)_2$, is coordinatively saturated and cannot accommodate the necessary C-H cleavage (oxidative addition) [5, 18].

The monohydride $\text{HIrCl}_2(\text{PCy}_3)_2$ (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 $\text{IrCl}_2(\text{PCy}_3)_2$ [4]. The hydride is also formed via addition of HCl to solutions of $[\text{IrCl}(\text{COT})]_2$ 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 $\nu(\text{Ir-H})$ 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 $\text{HIrCl}_2(\text{CO})(\text{PCy}_3)_2$, 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*- $\text{IrCl}(\text{CO})(\text{PCy}_3)_2$. Complex 4 has been characterized previously [$\nu(\text{CO}) = 2015$, $\nu(\text{IrH}) = 2276 \text{ cm}^{-1}$], having been made by reaction of $\text{IrCl}(\text{CO})(\text{PCy}_3)_2$ with HCl [4].



The $[\text{RhCl}(\text{COT})_2]_2/\text{PCy}_3$ systems were also studied by Vrieze *et al.* [9] and they noted formation of $\text{RhCl}[\text{P}(\text{C}_6\text{H}_9)\text{Cy}_2]_2(\text{PCy}_3)$ and $\text{H}_2\text{RhCl}(\text{PCy}_3)_2$, analogous to the iridium species. However, we find

that treatment of $[\text{RhCl}(\text{COT})_2]_2$ with PCy_3 in toluene at 20°C also yields $\text{HRhCl}_2(\text{PCy}_3)_2$ (Table I), which is more readily synthesized by treatment of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ with PCy_3 in acetone; this hydride has been made previously by reaction of HCl with $\text{RhCl}(\text{PCy}_3)_2$, 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 $\text{HRhCl}_2(\text{PCy}_3)_2$ complex.

Toluene solutions of the $[\text{MCl}(\text{COT})_2]_2$ complexes ($\text{M} = \text{Rh}, \text{Ir}$) 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 $\text{M}(\text{PCy}_3) + \text{CO}_2 \rightarrow \text{M}(\text{CO}) + \text{OPCy}_3$, [22]) although a band at 1755 cm^{-1} in the iridium system could be due to $\nu(\text{C=O})$ of coordinated CO_2 [23]. Carbon dioxide complexes of rhodium(I) have been synthesized by a similar procedure but using PBu_3 as the bulky phosphine [22]; few details were reported, but we found no evidence [24] for any reaction of $[\text{RhCl}(\text{olefin})_2]_2/\text{PBu}_3$ solutions with 1 atm CO_2 at 20°C (olefin = COT, C_2H_4).

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