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Preparation of Mono- or Di-metal Indenyl–Iridium Derivatives and of Tri-metal Iridium–Platinum Complexes**

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Abstract

Treatment of $[\mathrm{IrCl(C_2H_4)_4}]$ with $\mathrm{K(C_9H_7)}$ ($\mathrm{C_9H_7}$ = indenyl) gives $[\mathrm{Ir(C_2H_4)_2}(\eta\text{-}\mathrm{C_9H_7})]$. This compound is converted quantitatively into $[\mathrm{Ir(CO)_2}(\eta\text{-}\mathrm{C_9H_7})]$ by treatment with carbon monoxide. By reacting together these two iridium complexes $[\mathrm{Ir_2}(\mu\text{-}\mathrm{CO})(\mathrm{CO})_2(\eta\text{-}\mathrm{C_9H_7})_2]$ has been obtained. The compound $[\mathrm{Ir(CO)_2}(\eta\text{-}\mathrm{C_9H_7})]$ reacts with $[\mathrm{Pt(C_2H_4)_2}\{\mathrm{P(cyclo\text{-}C_6H_{11})_3}\}]$ to give the complex $[\mathrm{Ir_2Pt(CO)_3}\{\mathrm{P(cyclo\text{-}C_6H_{11})_3}\}(\eta\text{-}\mathrm{C_9H_7})_2]$. Protonation of the latter affords the salt $[\mathrm{Ir_2Pt}(\mu\text{-}\mathrm{H})(\mathrm{CO})_3\{\mathrm{P(cyclo\text{-}C_6H_{11})_3}\}(\mu\text{-}\mathrm{C_9H_7})_2][\mathrm{BF_4}]$. The main features of the molecular structure of these complexes have been established by IR and NMR spectroscopy.

Introduction

The isolobal relationship existing between carbenes $\mathrm{CR_2}$ on the one hand and 'carbene-like' metal–ligand fragments such as $\mathrm{M(CO)_5}$ (M = Cr, Mo, W), M(CO)L (M = Rh, Ir; L = η-$\mathrm{C_5Me_5}$, η-$\mathrm{C_9H_7}$), and $\mathrm{PtL_2}$ ($\mathrm{L_2}$ = cod = cyclo-octa-1,5-diene, or L = $\mathrm{PR_3}$ or CO) on the other [1] has enabled the synthesis of a variety of homo- or hetero-polynuclear transition metal derivatives to be rationalized [2–4].

The structures of some of these compounds can be regarded as the linkage of two 'methylene-like' metal fragments giving unsaturated species of the type $[\mathrm{MM'}(\mu\text{-}\mathrm{CO})_2(\eta\text{-}\mathrm{C_5Me_5})_2]$ (M = M′ = Co, Rh, Ir; M = Co, M′ = Rh, Ir; M = Rh, M′ = Ir) [5] which in some aspects behave as 'olefins', adding unsaturated metal centres isolobal with $\mathrm{CH_2}$ to give saturated clusters. Moreover $[\mathrm{Rh_2}(\mu\text{-}\mathrm{CO})_2(\eta\text{-}\mathrm{C_5Me_5})_2]$ displaces ethylene from $[\mathrm{Pt(C_2H_4)_3}]$ to give the pentanuclear cluster complex $[\mathrm{PtRh_4}(\mu\text{-}\mathrm{CO})_4(\eta\text{-}\mathrm{C_5Me_5})_4]$ [6]. It is also possible to use saturated compounds like $[\mathrm{M(CO)_2}(\eta\text{-}\mathrm{C_5Me_5})]$ (M = Rh, Ir) as precursors of cluster complexes having bonds between rhodium or iridium and other transition elements. Treatment of these rhodium and iridium species with metal–ligand groups with an affinity for CO leads to metal–metal bond formation, accompanied by transfer of CO from rhodium or iridium to another metal centre. Thus $[\mathrm{Rh(CO)_2}(\eta\text{-}\mathrm{C_5Me_5})]$ reacts with $[\mathrm{Pt(C_2H_4)_2(PPh_3)}]$ to give $[\mathrm{Rh_2Pt}(\mu\text{-}\mathrm{CO})_2(\mathrm{CO})(\mathrm{PPh_3})(\eta\text{-}\mathrm{C_5Me_5})_2]$ [3], or with the labile tetrahydrofuran (thf) complexes $[\mathrm{Mn(CO)_2(thf)}(\eta\text{-}\mathrm{C_5H_5})]$ and $[\mathrm{Cr(CO)_2(thf)}(\eta\text{-}\mathrm{C_6H_6})]$ to afford the dimetal compounds $[\mathrm{MnRh}(\mu\text{-}\mathrm{CO})_2(\mathrm{CO})_2(\eta\text{-}\mathrm{C_5H_5})(\eta\text{-}\mathrm{C_5Me_5})]$ and $[\mathrm{CrRh}(\mu\text{-}\mathrm{CO})_2(\mathrm{CO})_2(\eta\text{-}\mathrm{C_6H_6})(\eta\text{-}\mathrm{C_5Me_5})]$, respectively [4]. Moreover $[\mathrm{Ir(CO)_2}(\eta\text{-}\mathrm{C_5Me_5})]$ reacts with $[\mathrm{Pt(C_2H_4)_3}]$ to give the cluster complex $[\mathrm{Ir_3Pt_3}(\mu\text{-}\mathrm{CO})_3(\mathrm{CO})_3(\eta\text{-}\mathrm{C_5Me_4})_3]$ [7].

In order to extend the scope of these synthetic procedures we have studied the reactivity of the complex $[\mathrm{Ir(CO)_2}(\eta\text{-}\mathrm{C_9H_7})]$ with certain iridium and platinum complexes containing labile ligands. No indenyl derivatives of rhodium or iridium appear to have been previously used as starting materials in reactions of this type, but they have proved to be more reactive than the analogous pentamethylcyclopentadienyl complexes in reactions, for example, with molybdenum or tungsten alkylidyne compounds giving μ-alkylidyne heterobimetallic species [8].

To our knowledge a description of the synthesis and properties of the compounds $[\mathrm{IrL_2}(\eta\text{-}\mathrm{C_9H_7})]$ (L = $\mathrm{C_2H_4}$, CO) has not yet been reported and this has been included herein.

Experimental

Light petroleum refers to that fraction of boiling point range 40–60 °C. Experiments were carried out using Schlenck-tube techniques under a dry, oxygen free nitrogen atmosphere. All solvents were rigorously dried before use. The NMR measurements were made with JNM-FX 90Q and FX 200 instruments, and IR spectra were recorded with a Nicolet 10-MX FT spectrophotometer. The compounds $[\mathrm{IrCl(C_8H_{14})_2}]_2$ ($\mathrm{C_8H_{14}}$ = cyclooctene) [9] and $[\mathrm{Pt(C_2H_4)_2}\{\mathrm{P(cyclo\text{-}C_6H_{11})_3}\}]$ [10] were prepared as previously described.

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**Dedicated to Prof. Rafael Usón on his 60th birthday.

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Synthesis of the Compound [Ir(C_2H_4)$_2$(η-C_9H_7)] (1)

The complex [IrCl(C_2H_4)$_4$] was generated *in situ* by bubbling ethylene into a suspension of [IrCl(C_8H_{14})$_2$]$_2$ (3.8 g, 8.5 mmol) in light petroleum (30 cm^3) at 0 °C for 30 min as previously reported [11]. The mixture was cooled to −78 °C under ethylene and the solvent decanted off. A solution of K(C_9H_7) (9.5 mmol) in thf (30 cm^3) was added to the resulting white solid under nitrogen, the mixture being slowly warmed to room temperature for an hour. Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2 (50 cm^3) and filtered through an alumina pad (2 × 4 cm). The yellow solution was evaporated to dryness leaving a yellow solid, which was extracted with light petroleum (10 × 40 cm^3). These extracts were filtered through Celite, and the resulting solution concentrated to *ca.* 10 cm^3. By cooling to −20 °C overnight yellow crystals of **1** were obtained (1.82 g, 59% yield).

Synthesis of the Compound [Ir(CO)$_2$(η-C_9H_7)] (2)

Complex **1** (0.10 g, 0.28 mmol) was dissolved in light petroleum (20 cm^3) at room temperature, and a stream of CO was bubbled through the solution for 30 min. The yellow solution was evaporated and the resulting yellow solid dried *in vacuo* giving **2** quantitatively.

Synthesis of the Compound [Ir$_2$(μ-CO)(CO)$_2$(η-C_9H_7)$_2$] (3)

Compound **1** (0.10 g, 0.28 mmol) in n-hexane (30 cm^3) was treated with CO for 30 min. The solution was degassed by partial evaporation (until *ca.* 20 cm^3), and additional complex **1** (0.10 g, 0.28 mmol) was added. The mixture was stirred at about 40 °C for 2.5 h and, finally, refluxed overnight. Complex **3** precipitates as greenish-yellow crystals (0.071 g, 37%).

Synthesis of [Ir$_2$Pt(CO)$_3${P(cyclo-C_6H_{11})$_3$}(η-C_9H_7)$_2$] (4)

The compound **2** was generated from [Ir(C_2H_4)$_2$(η-C_9H_7)] (0.09 g, 0.24 mmol) and CO in Et_2O (10 cm^3). The resulting solution was added to [Pt(C_2H_4)$_2${P(cyclo-C_6H_{11})$_3$}] (0.013 g, 0.24 mmol) in Et_2O (5 cm^3) and the mixture was stirred at room temperature overnight. The solvent was removed *in vacuo*, and the residue extracted with light petroleum (3 × 15 cm^3). The extracts were applied to an alumina chromatography column (3 × 15 cm) charged with light petroleum. Elution with light petroleum-Et_2O (9:1) gave an orange band which, after removal of solvent *in vacuo*, yielded [Pt$_3$(μ-CO)$_3${P(cyclo-C_6H_{11})$_3$}$_3$] [12] (0.03 g, 25%). A dark green eluate was then obtained using the same solvents in 4:1 ratio. Removal of solvent *in vacuo* gave dark green microcrystals of **4** (0.09 g, 64% over Ir).

Protonation of [Ir$_2$Pt(CO)$_3${P(cyclo-C_6H_{11})$_3$}(η-C_9H_7)$_2$]

A solution of complex **4** (0.15 g, 0.13 mmol) in Et_2O (20 cm^3) was treated with a slight excess of HBF_4-diethylether. The solvent was decanted, and the precipitated salt washed with Et_2O (4 × 20 cm^3) and dried *in vacuo* yielding red–brown microcrystals of complex [Ir$_2$Pt(μ-H)(CO)$_3${P(cyclo-C_6H_{11})$_3$}(η-C_9H_7)$_2$][BF$_4$] (0.13 g, 80%).

Results and Discussion

The compound [Ir(C_2H_4)$_2$(η-C_9H_7)] (**1**) has been prepared by reaction of potassium indenyl with [IrCl(C_2H_4)$_4$], the latter being prepared *in situ* from [IrCl(C_8H_{14})$_2$]$_2$. This compound was identified by microanalysis and by its spectroscopic properties (Tables I and II). In particular the room temperature ^{1}H NMR spectrum showed two broad signals at about 0.85 and 2.89 ppm corresponding to fluxional ethylene ligands, which at a lower temperature (−50 °C) gave rise to two multiplet signals centered at 0.75 and 2.91 showing an *AA'BB'* pattern. This fluxional behaviour is similar to that previously described for the analogous Rh complex [13]. The compound is stable in air in the solid state.

When complex **1** is treated with carbon monoxide in solvents such as petroleum, CH_2Cl_2, Et_2O, or thf,

TABLE I. Analytical[a] and IR Data

Compound		ν(CO) (cm^{-1})[b]	Analysis (%)	
			C	H
1	[Ir(C_2H_4)$_2$(η-C_9H_7)]		43.0(43.0)	4.2(4.2)
2	[Ir(CO)$_2$(η-C_9H_7)]	2042vs, 1980vs	36.3(36.4)	2.0(1.9)
3	[Ir$_2$(μ-CO)(CO)$_2$(η-C_9H_7)$_2$]	1973vs, 1814m	36.4(36.1)	1.9(2.0)
4	[Ir$_2$Pt(CO)$_3${P(cyclo-C_6H_{11})$_3$}(η-C_9H_7)$_2$]	2001s, 1939vw, 1925vs	40.6(39.9)	4.2(4.0)
5	[Ir$_2$Pt(μ-H)(CO)$_3${P(cyclo-C_6H_{11})$_3$}(η-C_9H_7)$_2$][BF$_4$]	2063vs, 2004m, 1971vs[c]	37.4(37.1)	3.9(3.9)

[a] Calculated values are given in parentheses. [b] Measured in light petroleum, unless stated. [c] Measured in CH_2Cl_2.

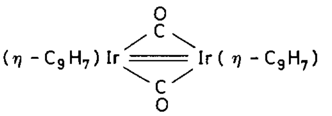
TABLE II. Hydrogen-1, Carbon-13 and Phosphorous-31 NMR Data[a]

Compound	$^1H(\delta)^b$	$^{13}C(\delta)^c$	$^{31}P(\delta)^b$
1	^{d}0.75, 2.91 (2xm, 8H, C_2H_4); 4.77 (d, 2H, H^2, C_9H_7, J(HH) 2.5); 5.72 (t, 1H, H^1, C_9H_7, J(HH) 2.5); 7.02 (m, 4H, H^3 and H^4, C_9H_7)	^{e}124.8, 120.6, 108.5, 83.3, 73.8 (C_9H_7), 24.1 (C_2H_4)	
2	^{e}5.08 (d, 2H, H^2, C_9H_7, J(HH) 3); 5.49 (t, 1H, H^1, C_9H_7, J(HH) 3); 6.87 (s, 4H, H^3 and H^4, C_9H_7)	^{e}171.7 (IrCO), 126.0, 119.7, 115.3, 93.6, 71.0 (C_9H_7)	
3	^{f}5.31 (d, 4H, C_9H_7, J(HH) 3); 5.93 (t, 2H, C_9H_7, J(HH) 3); 6.9–7.3 (m, 8H, C_9H_7)	^{g}193.9 (μ-CO), 172.1 (IrCO), 128–73 (C_9H_7)	
4	1.3–2.0 (m, 33H, P(cyclo-$C_6H_{11})_3$); 5.3–5.7 (m, 6H, C_9H_7); 6.6–7.1 (m, 8H, C_9H_7)	^{h}177.8 (IrCO), 176.8(d, IrCO, J(PC) 7), 162.9 (d, PtCO, J(PC) 10), 124–67 (C_9H_7), 39–25 (P(cyclo-$C_6H_{11})_3$)	28.6 (s, J(PtP) 2637
5	−12.28 (d, 1H, μH, J(PH) 9, J(PtH) 529); 1.2–2.0 (m, 33H, P(cyclo-$C_6H_{11})_3$); 5.1–6.2 (m, 6H, C_9H_7); 7.1–7.5 (m, 8H, C_9H_7)	^{h}171.5 (IrCO), 170.3 (IrCO); 166.5 (d, PtCO, J(PC) 6, J(PtC) 1820), 130–70 (C_9H_7), 38–26 (P(cyclo-$C_6H_{11})_3$)	38.5 (s, J(PtP) 2332)

[a] Chemical shifts (δ) in ppm, coupling constants in Hz, measurements at ambient temperature unless otherwise stated. Chemical shifts are positive to a high frequency of $SiMe_4$ (^{13}C [^1H]) and PO_4H_3 (^{31}P [^1H]). [b] Measured in $CDCl_3$ unless otherwise stated. [c] Measured in CH_2Cl_2/CD_2Cl_2 unless otherwise stated. [d] Measured in C_6D_6 at room temperature and in $C_6D_5CD_3$ at −50 °C. See text. [e] Measured in C_6D_6. [f] Measured in CD_2Cl_2. [g] Measured at −70 °C. [h] Measured at −30 °C.

both ethylene groups are displaced giving the dicarbonyl compound [$Ir(CO)_2(\eta$-$C_9H_7)$] (2) which could be obtained in the solid state by removing the solvent *in vacuo*. Data for 2 are summarised in Tables I and II.

We have studied the reaction between 1 and 2 in an attempt to obtain an unsaturated species such as A. This procedure has previously proved to be useful



$(\eta - C_9H_7)\,Ir(\mu\text{-}CO)_2Ir(\eta - C_9H_7)$

A

for the synthesis of homo- and heteronuclear complexes of the type [$MM'(\mu$-$CO)_2(\eta$-$C_5Me_5)_2$] (M, M′ = Co, Rh, Ir) [5]. Nevertheless the presence of the indenyl groups does not appear to stabilize this unsaturated molecule and instead the saturated dimetal compound [$Ir_2(\mu$-$CO)(CO)_2(\eta$-$C_9H_7)_2$] (3) is formed in moderate yield. We propose the structure shown in Fig. 1 on the basis of analysis, IR and NMR data Tables I and II). The IR spectrum showed an absorption at 1814 cm^{-1} suggesting the presence of a bridging CO ligand and another band at 1973 cm^{-1}. These data support the *trans* disposition of the CO ligands about the metal–metal bond, similar to that found earlier in [$Rh_2(\mu$-$CO)(CO)_2(\eta$-$C_5H_5)_2$] [14]. In the carbonyl region of its ^{13}C [^1H] NMR spectrum, two signals are observed at 193.9 and 172.1 ppm, the latter having a higher peak intensity than the former, confirming the presence of one bridging and two terminal carbonyl groups.

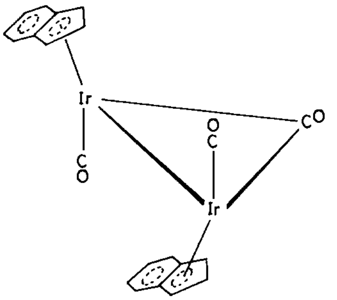


Fig. 1. Proposed structure for complex 3.

Compound 3 is unstable in solution, decomposing quickly in acetone and chloroform and more slowly in dichloromethane to give unidentified species. It is thus necessary to measure the ^{13}C NMR spectrum at low temperature.

Iridium–Platinum Compounds

By reaction of [$Ir(CO)_2(\eta$-$C_9H_7)$] with a mol equivalent of [$Pt(C_2H_4)_2\{P(cyclo$-$C_6H_{11})_3\}$] in Et_2O, followed by chromatography of the resulting mixture a first fraction of the known compound [12] [$Pt_3(\mu$-$CO)_3\{P(cyclo$-$C_6H_{11})_3\}_3$] is obtained. Elution with light petroleum–Et_2O mixtures affords a dark green solution, which after removal of the solvent yields the

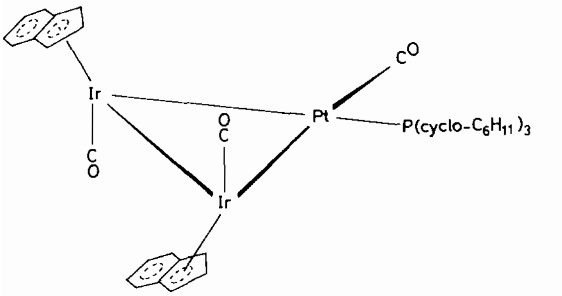


Fig. 2. Proposed structure for complex **4**.

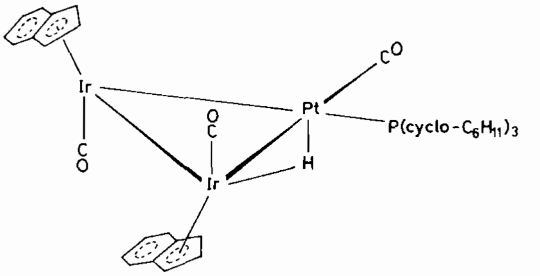


Fig. 3. Proposed structure for the cation **5**.

new heterotrimetallic cluster $[Ir_2Pt(CO)_3\{P(cyclo\text{-}C_6H_{11})_3\}(\eta\text{-}C_9H_7)_2]$ (**4**). The ^{13}C [^1H] NMR spectrum of the latter shows singlet and doublet resonances at 177.8 and 176.8 ppm, respectively, in the same chemical shift region at which terminal Ir–CO ligands resonate in compounds **2** and **3**. The doublet arises from coupling through three bonds with a *trans* phosphorous atom. A further peak is observed as a doublet at 162.9 ppm [$J(PC) = 10$ Hz] as expected for a CO group bonded to the platinum atom in a *cis* position with respect to the phosphine ligand. The ^{31}P NMR spectrum shows a resonance at 28.6 ppm with platinum satellites [$J(PtP) = 2637$ Hz] which confirms the coordination of the $P(cyclo\text{-}C_6H_{11})_3$ group to the platinum atom. The IR spectrum of **4** in the carbonyl region shows one medium intensity band at 2001 cm^{-1}, assigned to a terminal CO bonded to platinum; a very weak absorption at 1939 cm^{-1} and a further strong absorption at 1925 cm^{-1} are assigned to the symmetric and asymmetric stretching vibration of two mutually *trans* disposed terminal CO groups bonded to the iridium atoms. These data strongly imply the structure depicted in Fig. 2, with a planar arrangement at the platinum atom. Perhaps the most important structural feature in this complex is the lack of bridging CO groups, in contrast with the previously reported compound $[PtRh_2(\mu\text{-}CO)_2(CO)(PPh_3)(\eta\text{-}C_5Me_5)_2]$ [3] which was shown (by X-ray diffraction studies) to have two CO ligands triply bridging the two rhodium atoms and the platinum. Thus the *trans* CO arrangement present in the di-iridium complex **3** is maintained in **4**, with the bridging CO ligand replaced by a bridging $Pt(CO)\{P(cyclo\text{-}C_6H_{11})_3\}$ fragment. Compound **4** can be viewed as the result of the coordination of an 'ethylene-like' Ir = Ir fragment to an unsaturated $Pt(CO)\{P(cyclo\text{-}C_6H_{11})_3\}$ species isolobal with CH_2. No Ir–Pt cluster complexes without bridging ligands appear to have been previously obtained.

Finally, treatment of **4** with a slight excess of HBF_4 in Et_2O affords a precipitate of the red–brown salt $[Ir_2Pt(\mu\text{-}H)(CO)_3\{P(cyclo\text{-}C_6H_{11})_3\}(\eta\text{-}C_9H_7)_2][BF_4]$. Spectral data (IR, ^{13}C NMR and ^{31}P NMR) (Tables I and II) are similar to those observed for complex **4**, indicating no changes in the gross aspects of the structure. The ^1H NMR spectrum exhibits a doublet signal at -12.3 ppm [$J(PH) = 9$ Hz], with platinum satellites [$J(PtH) = 529$ Hz]. These data are in agreement with the presence of a hydrogen atom bridging one of the platinum–iridium atoms, in a *cis* position with respect to the phosphine ligand (Fig. 3). This reaction is similar to that observed for the protonation of $[Rh_2Pt(\mu\text{-}CO)_2(CO)(PPh_3)(\eta\text{-}C_5Me_5)_2]$ [15]. The difference, again, arises from the fact that complex **5** has terminal carbonyl groups, while the pentamethylcyclopentadienyl Rh_2Pt derivative has two bridging carbonyl ligands.

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