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SOME TRANSESTERIFICATION REACTIONS OF $[Ir(CO_2Me)(CO)_2(PPh_3)_2]$

P.J. FRASER, W.R. ROPER and F.G.A. STONE*
Department of Inorganic Chemistry, The University, Bristol BS8 1TS (Great Britain)
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Summary

The iridium(I) complex $[Ir(CO_2Me)(CO)_2(PPh_3)_2]$ undergoes a transesterification reaction with the alcohols $CH_2{=}C(R)CH_2OH$ ($R = H, Me$), $MeC{\equiv}CCH_2CH_2OH$, and $HOCH_2CH_2OH$ to afford the complexes $[Ir(CO_2CH_2CR{=}CH_2)(CO)(PPh_3)_2]$, $[Ir(CO_2CH_2CH_2{\equiv}CMe)(CO)_2(PPh_3)_2]$ and $[Ir(CO_2CH_2CH_2OH)(CO)_2(PPh_3)_2]$, respectively. In contrast the acetylenic alcohol $HC{\equiv}CCH_2CH_2OH$ gives $[Ir(C{\equiv}CCH_2CH_2OH)(CO)PPh_3)_2]$. Some reactions of the new complexes are described.

Introduction

The chemistry of transition metal alkoxycarbonyl complexes has been reviewed recently [1]. These compounds are generally obtained by treating carbonylmetal anions with chloroformate esters, or by alkoxide ion attack on carbonylmetal cations. The latter method has been used to prepare alkoxycarbonyls of Ir^I and Ir^{III} [2 - 7]. Alkoxycarbonyls of Ir^{III} have also been obtained by oxidative-addition of chloroformate esters to Ir^I compounds [8].

Herein we describe some Ir^I alkoxycarbonyl complexes obtained by reacting $[Ir(CO_2Me)(CO)_2(PPh_3)_2]$ (I) [2] with various alcohols. The synthesis is analogous to the well known transesterification reaction in organic chemistry, and has been previously shown to occur for a Pt^{II} alkoxycarbonyl compound [9].

Results and discussion

The complex $[Ir(CO_2Me)(CO)_2(PPh_3)_2]$ (I) reacts with the alcohols $CH_2{=}CRCH_2OH$ ($R = H, Me$), $MeC{\equiv}CCH_2CH_2OH$, and $HOCH_2CH_2OH$ to afford the alkoxycarbonyl complexes $[Ir(CO_2CH_2CR{=}CH_2)(CO)(PPh_3)_2]$ [(II) $R = H$; (III) $R = Me$], $[Ir(CO_2CH_2CH_2C{\equiv}CMe)(CO)_2(PPh_3)_2]$ (IV) and $[Ir(CO_2CH_2CH_2OH)(CO)_2(PPh_3)_2]$ (V), respectively. In contrast the acetylenic

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* Author to whom correspondence should be addressed.

TABLE 1

IR[a](cm^{-1}) AND ^1H NMR[b](τ) DATA FOR THE IRIDIUM COMPLEXES

Complex		$\nu(CO)$	$\nu(\underset{\underset{\textstyle O}{\|}}{C}OR)$	Other bands	Chemical shifts[c]
(I)	$[Ir(CO_2Me)(CO)_2(PPh_3)_2]$	1993, 1944	1638		OMe, 7.10s; PPh, 2.73m
(II)	$[Ir(CO_2CH_2CH{=}CH_2)(CO)(PPh_3)_2]$	2005	1667		$C{=}CH_2$, 8.37m, 7.60m; OCH_2, 6.68m; CH=C, 6.07m; PPh, 2.77m.
(III)	$[Ir(CO_2CH_2CMe{=}CH_2)(CO)(PPh_3)_2]$	1987	1666		CMe, 8.58m; $C{=}CH_2$, 8.58m, 8.01m; OCH_2, 6.47m, 6.37m, PPh, 2.73m
(IV)	$[Ir(CO_2(CH_2)_2C{\equiv}CMe)(CO)_2(PPh_3)_2]$[d]	1984, 1933	1648		CMe, 8.32t[e]; $(CH_2)_2$, 8.15m, 6.70t[f]; PPh, 2.78m.
(V)	$[Ir(CO_2(CH_2)_2OH)(CO)_2(PPh_3)_2]$	1999, 1946	1639	$\nu(OH)$ 3340	OH, 7.15br; $(CH_2)_2$, 6.59t[g], 6.35t[g]; PPh, 2.63m
(VI)	$[Ir(C{\equiv}C(CH_2)_2OH)(CO)(PPh_3)_2]$	1968		$\nu(OH)$ 3540 $\nu(C{\equiv}C)$ 2104	OH, 8.57br; $(CH_2)_2$, 7.77t[h], 6.90t[h]; PPh, 2.48m

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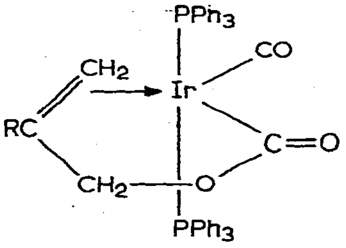
[a] Nujol mull. [b] $CDCl_3$ solution. [c] s, singlet; t, triplet; m, multiplet; br, broad. [d] $\nu(C{\equiv}C)$ not discernible. [e] $^5J(HH)$ 2Hz. [f] $^3J(HH)$ 8Hz. [g] $^3J(HH)$ 7Hz. [h] $^3J(HH)$ 6Hz.

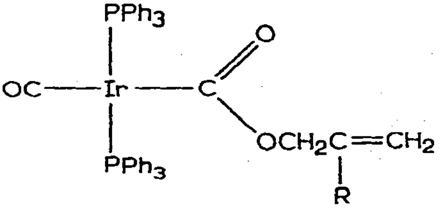
alcohol $HC{\equiv}CCH_2CH_2OH$ gives the iridium acetylide complex $[Ir(C{\equiv}CCH_2CH_2OH)(CO)(PPh_3)_2]$ (VI).

Compounds (II)—(VI) can also be prepared by reacting the salt $[Ir(CO)_3(PPh_3)_2][ClO_4]$ (VII) [10] with the appropriate alcohol in the presence of base. In the case of $HOCH_2CH_2OH$, the hydrido complex $[IrH(CO)_2(PPh_3)_2]$ (VIII) [11] was also isolated from the reaction mixture. Reaction of either (I) or (VII) with $Cl(CH_2)_nOH$ ($n = 2,3$) in the presence of base gave Vaska's complex $[IrCl(CO)(PPh_3)_2]$.

The IR and NMR data for the new compounds are given in Table 1. Analytical and IR spectroscopic (see Table 1) data indicate that (II) and (III) contain a single terminal carbonyl group, as well as an alkoxycarbonyl moiety. Two structures can be postulated for these complexes: (A) a chelate olefin structure, or (B) a four-coordinate square planar structure with a free olefinic group. Structure (A) is favoured for the two compounds because of the observed relatively high carbonyl stretching frequencies compared with those found in the spectra of four-coordinate Ir^I complexes [12], coupled with the absence of a free carbon—carbon double bond stretch. Moreover, the increased shielding (about 3.3 ppm) of the olefinic methylene protons (see Table 1) in the proton NMR spectra of (II) and (III) compared with those in the free ligands [13,14] strongly indicates olefin coordination.



(A)



(B)

Complexes (IV) and (V) both show two terminal carbonyl stretching bands in their IR spectra, together with a band due to the acyl group. These complexes undoubtedly have a trigonal bipyramidal structure similar to that postulated [2,7] for (I), which has very similar carbonyl and acyl stretching bands in its IR spectrum (Table 1). In contrast, complex (VI) shows a single CO stretching frequency in its IR spectrum, typical of a square planar Ir^I compound, and no band characteristic of an alkoxycarbonyl moiety. The spectrum did show bands due to $\nu(OH)$ and $\nu(C{\equiv}C)$, and the properties of the compound are similar to those of other recently prepared acetylide complexes $[Ir(C{\equiv}CR)(CO)(PPh_3)_2]$ [15 - 17].

Alkoxycarbonyl complexes afford metal carbonyl compounds on treatment with acids [1], and compound (II) was found to react with fluoroboric or perchloric acids to give salts $[Ir(CO)_3(PPh_3)_2]X$ ($X = BF_4$, ClO_4) (VII) in about 40% yield. Presumably these species arise via decomposition of initially formed $[Ir(CO)_2(PPh_3)_2]X$. The salt (VII) ($X = BF_4$) is also formed when (II) is treated with $[Ph_3C]BF_4$ or $[Me_3O]BF_4$. Similarly, treatment of (V) with perchloric acid affords (VII) ($X = ClO_4$), and reaction of (I) with $[Me_3O]BF_4$ or $[Ph_3C]BF_4$ in dichloromethane also gives (VII) ($X = BF_4$).

Reaction of compound (II) with methyl iodide leads to initial formation of $[IrI(CO)_2(PPh_3)_2]$ [5], but prolonged reaction affords the known Ir^{III} oxidative-addition product $[IrI_2Me(CO)(PPh_3)_2]$ [18].

The fact that the reaction of (II) and methyl iodide gives the dicarbonyl $[IrI(CO)_2(PPh_3)_2]$ possibly indicates that the C(O)—OR bond of (II) is cleaved by methyl iodide rather than the Ir—C bond. This result can be contrasted with that observed for anionic nickel carbamoyl derivatives where the nickel—carbon bond is cleaved by alkyl halides, not the carbon—nitrogen bond [19].

Reaction of (II) with bromine gives the Ir^{III} complex $[IrBr_3(CO)(PPh_3)_2]$ [20]. Whether (II) reacts with bromine via cleavage of the Ir—C or C(O)—OR bond is not obvious. However, cleavage of the metal—carbon bond of transition metal carbamoyl derivatives occurs with bromine [21].

Complex (II) does not react with carbon monoxide, nor with triphenylphosphine, and this contrasts with the behaviour of $(\sigma + \pi)$ allyl complexes of Rh^{III}, where the olefin moiety can be displaced by carbon monoxide [22].

No reaction was observed when (II) was treated with methyllithium, whereas King et al. [23] found that the alkoxycarbonyl complex $[Fe(CO_2Me)(CO)_2(C_5H_5)]$ reacts with methylmagnesium bromide to give the acyl complex $[Fe(COMe)(CO)_2(C_5H_5)]$.

Experimental

^1H NMR spectra were recorded on Varian Associates T 60 and HA 100 spectrometers. IR spectra were recorded with a Perkin—Elmer 457 spectrophotometer. Solvents were dried and distilled under nitrogen, and all operations were conducted in an atmosphere of dry oxygen-free nitrogen. The cationic iridium complex $[Ir(CO)_3(PPh_3)_2][ClO_4]$ (VII) was prepared by passing carbon monoxide through an equimolar suspension of $[IrCl(CO)(PPh_3)_2]$ and sodium perchlorate in acetone [10]. The Malatesta [2] compound $[Ir(CO_2Me)(CO)_2(PPh_3)_2]$ (I) was prepared as follows.

A stoichiometric amount of sodium methoxide in methanol (1 ml) was added slowly to a stirred suspension of (VII) (0.45 g, 0.5 mmol) in tetrahydrofuran (5 ml). A clear, light yellow solution was obtained which, after 0.5 h, was evaporated to dryness. The solid remaining was extracted with benzene and the solution was filtered. Slow addition of light petroleum gave white needles of (I) (0.34 g, 82%). (Found: C, 57.8; H, 4.1. $C_{40}H_{33}IrO_4P_2$ calcd.: C, 57.7; H, 4.0%.)

Synthesis of new compounds

(*a*) $[Ir(CO_2CH_2CH{=}CH_2)(CO)(PPh_3)_2]$ (II) was prepared by treating (I) (0.25 g, 0.3 mmol) with excess allyl alcohol (0.5 ml) in benzene (10 ml) for 0.5 h. Slow addition of hexane gave white crystals of (II) (0.20 g, 78%), m.p. 164 - 166° (decomp.). (Found: C, 59.5; H, 4.0. $C_{41}H_{35}IrO_3P_2$ calcd.: C, 59.3, H, 4.3%.)

(*b*) $[Ir(CO_2CH_2CMe{=}CH_2)(CO)(PPh_3)_2]$ (III) was similarly prepared in 80% yield, as white crystals m.p. 146.5 - 147.5° (decomp.). (Found: C, 60.0; H, 4.3. $C_{42}H_{37}IrO_3P_2$ calcd.: C, 59.8; H, 4.4%.)

(*c*) $[Ir(CO_2CH_2CH_2C{\equiv}CMe)(CO)_2(PPh_3)_2]$ (IV) was obtained similarly from (I) and $MeC{\equiv}CCH_2CH_2OH$ in 71% yield as white crystals m.p. 130 - 140° (decomp. with gas evolution). (Found: C, 59.9; H, 4.4. $C_{44}H_{37}IrO_4P_2$ calcd.: C, 59.8; H, 4.2%.)

(*d*) $[Ir(CO_2CH_2CH_2OH)(CO)_2(PPh_3)_2]$ (V) was synthesized from (I) and $HOCH_2CH_2OH$ in 60% yield, white crystals m.p. 135 - 140° (decomp.). (Found: C, 56.9; H, 4.2. $C_{41}H_{35}IrO_5P_2$ calcd.: C, 57.1; H, 4.1%.)

(*e*) $[Ir(C{\equiv}CCH_2CH_2OH)(CO)(PPh_3)_2]$ (VI) was prepared by treating (I) with $HC{\equiv}CCH_2CH_2OH$, and obtained in 45% yield, as yellow crystals, m.p. 144 - 146°. (Found: C, 60.2; H, 4.0. $C_{41}H_{35}IrO_2P_2$ calcd.: C, 60.5; H, 4.3%.)

Reactions of complex (I)

(a) With 2-chloroethanol. Treatment of (I) (0.25 g, 0.30 mmol) in dry benzene (10 ml) with freshly distilled 2-chloroethanol (0.5 ml) gave yellow crystals of $[IrCl(CO)(PPh_3)_2]$ (0.17 g, 72%) after 16 h, identified by its infrared spectrum.

(b) With 3-chloropropanol. Treatment of (I) (0.15 g, 0.18 mmol) in dry benzene (10 ml) with freshly distilled 3-chloropropanol (0.5 ml) gave yellow crystals of $[IrCl(CO)(PPh_3)_2]$ (0.13 g, 92%) after 4 h, identified by its infrared spectrum.

(c) With trityl fluoroborate. Treatment of (I) (0.19 g, 0.23 mmol) in dichloromethane (5 ml) with $[Ph_3C][BF_4]$ (0.08 g, 0.24 mmol) for 3 h gave, on addition of hexane, a white solid which was recrystallized from chloroform—hexane to give white crystals of (VII) ($X = BF_4$), isolated as a chloroform solvate (0.06 g, 30%). (Found: C, 47.5; H, 3.1. $C_{40}H_{31}BCl_3F_4IrP_2O_3$ calcd.: C, 47.7; H, 3.3%.) $\nu(CO)$ (Nujol) 2080 w, 2024 s, 1997 s cm^{-1}.

(d) With trimethyloxonium fluoroborate Treatment of (I) (0.20 g, 0.24 mmol) in dichloromethane (5 ml) with a stoichiometric amount of $[Me_3O]BF_4$ for 0.5 h gave, on addition of hexane, a white solid, which was recrystallised from chloroform—hexane and identified as (VII) ($X = BF_4$) (0.18 g, 76%), identified by comparison of its infrared spectrum with that of the product in (*c*) above.

Reaction between (VII) and 2-chloroethanol

To a stirred suspension of freshly distilled 2-chloroethanol (2 ml) and $[Ir(CO)_3(PPh_3)_2][ClO_4]$ (VII) (0.45 g, 0.5 mmol) in tetrahydrofuran was added a small amount of powdered potassium hydroxide. A yellow solution was obtained which, on evaporation and recrystallization from dichloromethane/hexane, gave yellow crystals of $[IrCl(CO)(PPh_3)_2]$ (0.26 g, 66%), identified by its infrared spectrum.

Reactions of complex (II)

(a) With fluoroboric acid. A stoichiometric amount of HBF_4 in tetrahydrofuran was added slowly to a stirred tetrahydrofuran solution of (II) (0.09 g, 0.11 mmol). After 0.75 h, solvent was removed and the solid extracted with dichloromethane (2 ml). Slow addition of petrol gave white crystals of (VII) ($X = BF_4$) (0.04 g, 37%), identified by its infrared spectrum.

A similar reaction of (II) with $HClO_4$ gave the perchlorate salt of (VII) in 41% yield.

(b) With trityl fluoroborate. $[Ph_3C][BF_4]$ (0.07 g, 0.21 mmol) in dichloromethane (5 ml) was added slowly to a stirred solution of (II) (0.17 g, 0.20 mmol) in dichloromethane (10 ml). After 15 min light petroleum was added giving white crystals of (VII) ($X = BF_4$) (0.10 g, 46%).

(c) With trimethyloxonium fluoroborate. Treatment of (II) (0.20 g, 0.24 mmol) with a stoichiometric amount of $[Me_3O]BF_4$ in dichloromethane (10 ml) for 0.5 h gave, on addition of hexane, a white solid, which was recrystallised from chloroform—hexane and identified as (VII) ($X = BF_4$), crystallising as a chloroform solvate, and identified by its infrared spectrum.

(d) With methyl iodide. Addition of methyl iodide (2 ml) to a sample of (II) (0.10 g, 0.12 mmol) and stirring for 6 h gave, after removal of solvent, a yellow oil, which afforded on crystallisation (dichloromethane—ethanol) $[IrI(CO)_2(PPh_3)_2]CH_2Cl_2$ (0.07 g, 59%). (Found: C, 47.9; H, 3.3. $C_{39}H_{32}Cl_2IIrO_2P_2$ calcd.: C, 47.6; H, 3.3%.) ν(CO) (Nujol) 1984 s, 1928 vs cm^{-1} (lit. [5] ν(CO) 1990 and 1930 cm^{-1}).

The reaction between (II) (0.15 g, 0.18 mmol) and methyl iodide (2 ml) was repeated for 16 h. The yellow solid obtained was crystallised from dichloromethane—ethanol to give needles of $[IrI_2Me(CO)(PPh_3)_2]$ (0.12 g, 65%). (Found: C, 45.2; H, 3.6. $C_{38}H_{33}I_2IrOP_2$ calcd.: C, 45.1; H, 3.3%.) ν(CO) (Nujol) 2029 vs cm^{-1} ν(CO)(CH_2Cl_2) 2040 vs cm^{-1} (lit. [18] 2045 cm^{-1} (tetrahydrofuran)).

(e) With bromine. A slight excess of bromine in carbon tetrachloride was added slowly to a stirred solution of (II) (0.26 g, 0.31 mmol) in dichloromethane (10 ml). After 1 h solvent was removed, and the solid remaining was recrystallised from methanol to give $[IrBr_3(CO)(PPh_3)_2]$ (0.28 g, 77%) ν(CO) (Nujol) 2074 vs cm^{-1} (lit. [20] ν(CO) 2076 cm^{-1}).

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