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Synthesis and reactions of phenylacetylide iridium(I) and rhodium(I) complexes

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Abstract

The complexes $Ir(C{\equiv}CPh)(cod)(PPh_3)_2$ and $Rh(C{\equiv}CPh)(cod)(PCy_3)$ (cod = cycloocta-1,5-diene; Cy = cyclohexyl) have been prepared by reaction of the corresponding $[M(\mu\text{-}OMe)(cod)]_2$ dimers with PPh_3 or PCy_3 and $HC{\equiv}CPh$. $Ir(C{\equiv}CPh)(cod)(dppe)$ (dppe = $Ph_2PCH_2CH_2PPh_2$) has been made by treatment of $Ir(C{\equiv}CPh)(cod)(PCy_3)$ with dppe, and $M(C{\equiv}CPh)(CO)(PCy_3)_2$ (M = Ir, Rh) have been made by carbonylation of the diolefin $M(C{\equiv}CPh)(cod)(PCy_3)$ compounds in the presence of PCy_3. The preparation of the related dicarbonyl $Ir(C{\equiv}CPh)(CO)_2(dppe)$ complex by reaction of $Ir(C{\equiv}CPh)(cod)(dppe)$ with carbon monoxide is also reported. $Ir(C{\equiv}CPh)(CO)_2(dppe)$ reacts with hydrogen to give the dihydrido complex $IrH_2(C{\equiv}CPh)(CO)(dppe)$.

Introduction

Interest in the preparation of σ-alkynylmetal complexes is enhanced by the suggested involvement of this type of species in some catalytic reactions involving alkynes [1,2]. Although in the past decade several σ-alkynyl-Vaska-type compounds of iridium and the related oxidative addition products have been described [3,4], the number of such complexes remains small.

During our recent work on the chemistry of systems derived from the reaction of $[Ir(\mu\text{-}OR)(cod)]_2$ (cod = cycloocta-1,5-diene, R = alkyl) with Group 15 atom donor ligands [5–8], we found that terminal alkoxide species are initially formed [8]. Use of these terminal alkoxide species may provide an easy route to different types of complex. As part of this work, we report here the synthesis and reactivity of new phenylacetylide-iridium(I) and -rhodium(I) complexes.

Results and discussion

The synthesis of $Rh(C{\equiv}CPh)(cod)(PCy_3)$ involves a straightforward reaction in diethyl ether between $[Rh(\mu\text{-}OMe)(cod)]_2$, PCy_3 and $HC{\equiv}CPh$, in a $Rh/P/HC{\equiv}CPh$

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ratio of 1/1/1 according to eq. 1. The compound was obtained as a yellow,

$$[Rh(\mu\text{-}OMe)(cod)]_2 + 2\ PCy_3 + 2\ HC{\equiv}CPh \rightarrow$$
$$2\ Rh(C{\equiv}CPh)(cod)(PCy_3) + 2\ MeOH \quad (1)$$

air-stable, powder in good yield (75%). Formulation of the complex is supported by microanalysis, ^{1}H NMR, and IR data. The ^{1}H NMR spectrum shows two broad signals at 4.16 and 5.34 ppm for the vinyl (cod) protons, in keeping with a square-planar geometry. The IR spectrum shows a strong absorption at 2081 cm^{-1}, attributable to $\nu(C{\equiv}C)$, in keeping with the coordination of a σ-phenylacetylide ligand.

We examined the reaction of $[Ir(\mu\text{-}OMe)(cod)]_2$ with PPh_3 and HC≡CPh, in a Ir/P/HC≡CPh ratio of 1/1/1, in diethyl ether. Under these conditions a red solid was obtained, but its low stability prevented its characterization, and so we monitored the reaction by ^{1}H NMR spectroscopy in $CDCl_3$. The ^{1}H NMR spectrum of the final red solution is consistent with the formation of the square-planar $Ir(C{\equiv}CPh)(cod)(PPh_3)$ complex; it shows a singlet at 3.45 ppm attributable to free methanol, two broad signals at 5.25 and 3.20 ppm due to the vinyl (cod) protons, and complex aliphatic (δ 1.7–2.2 ppm) signals arising from the cod ligand. Additional signals (δ 6.7–7.9 ppm) are assigned to the aromatic protons of the PPh_3 and C≡CPh groups.

When the reaction of $[Ir(\mu\text{-}OMe)(cod)]_2$ with PPh_3 and HC≡CPh was carried out in a Ir/P/HC≡CPh ratio of 1/2/1, in diethyl ether, the $Ir(C{\equiv}CPh)(cod)(PPh_3)_2$ complex was obtained as a white, air-stable, powder. The microanalysis, ^{1}H NMR, and IR data were consistent with the proposed formulation. The ^{1}H NMR spectrum exhibits a single signal at 3.65 ppm for the vinyl (cod) protons resonance, typical of a fluxional pentacoordinated iridium(I) complex [9]. The IR spectrum shows a band at 2106 cm^{-1} attributable to $\nu(C{\equiv}C)$.

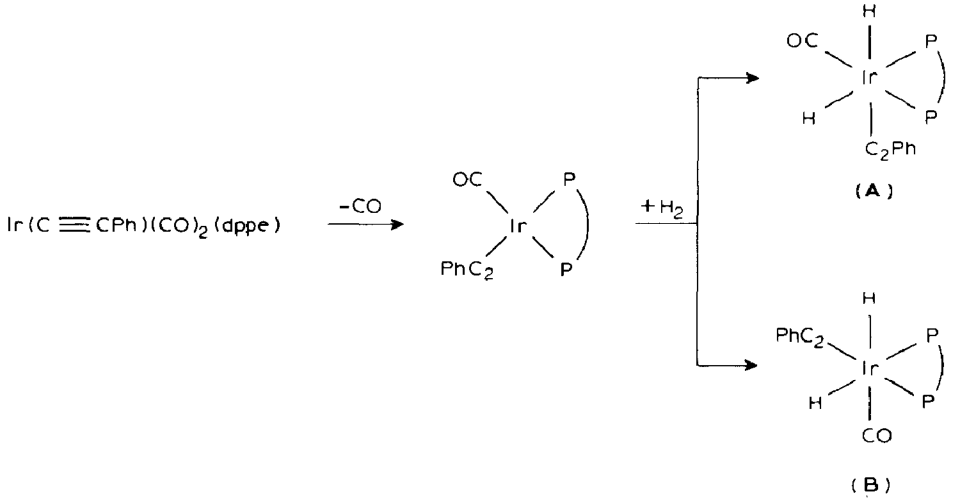
Reaction of $Ir(C{\equiv}CPh)(cod)(PCy_3)$ with dppe (dppe = $Ph_2PCH_2CH_2PPh_2$) results in exchange of PCy_3 for dppe to give Ir(C≡CPh)(cod)(dppe). The formulation of the product is supported by microanalyses and IR data. Ir(C≡CPh)(cod)(dppe) cannot be prepared by reaction of $[Ir(\mu\text{-}OMe)(cod)]_2$ with dppe and HC≡CPh, which gives an unsolved mixture of products. Formation of Ir(C≡CPh)(cod)(dppe) in the latter reaction could be inhibited by the tendency of the dppe ligand to form bis-chelate complexes [10–12], or by the occurrence of a more complex reaction between HC≡CPh and the hypothetical coordinatively-saturated Ir(OMe)(cod)(dppe) intermediate.

The carbonylated $M(C{\equiv}CPh)(CO)(PCy_3)_2$ (M = Ir, Rh) complexes were made by reaction of $M(C{\equiv}CPh)(cod)(PCy_3)$ with carbon monoxide in the presence of one equivalent of PCy_3. $Ir(C{\equiv}CPh)(CO)_2(dppe)$ and the known $Ir(C{\equiv}CPh)(CO)_2(PPh_3)_2$ [3] were prepared by displacement of the cod ligand from $Ir(C{\equiv}CPh)(cod)L_2$ (L = PPh_3, dppe) with carbon monoxide. The products were characterized by microanalysis and IR spectroscopy.

$Ir(C{\equiv}CPh)(CO)_2(dppe)$ undergoes oxidative addition of H_2 to give the white, air-stable complex $IrH_2(C{\equiv}CPh)(CO)(dppe)$ (eq. 2). The complex was characterized by microanalysis and ^{1}H NMR and IR spectroscopy. The ^{1}H NMR spectrum shows two hydride resonances, which suggests that the isolated solid contains only one dihydride isomer. These resonances appear as a triplet at -10.37 (J(H–P) 19.0 Hz) and a doublet of doublets at -9.60 ppm (J(H–P) 137.8, 13.3 Hz), indicating that one hydride is *cis* to both phosphorus atoms and the other is *trans* to one phosphorus and *cis* to the second phosphorous.

As portrayed in eq. 2, we believe that the formation of $\mathrm{IrH_2(C{\equiv}CPh)(CO)(dppe)}$ involves a *cis*-addition procces of H_2 to the square planar $\mathrm{Ir(C{\equiv}CPh)(CO)(dppe)}$ intermediate, formed by dissociation of CO from the initial $\mathrm{Ir(C{\equiv}CPh)(CO)_2(dppe)}$ complex. Eisenberg et al. [12–14] have studied the oxidative addition of H_2 to the analogous IrX(CO)(dppe) (X = Cl, Br, I, CN, H) complexes. In accord with their work, two diastereomers (**A** and **B**, eq. 2) could be formed (in the *cis*-addition of H_2 to this type of compounds).

The ^{1}H NMR and IR data for the isolated $\mathrm{IrH_2(C{\equiv}CPh)(CO)(dppe)}$ do not permit us to decide between structures **A** or **B** for this compound.



(2)

The results reported by us in this work and previously [8] show that that alkoxide compounds are useful starting materials for the synthesis of σ-alkynyl complexes. They also confirm the versatility of the chemistry of the systems $[\mathrm{M}(\mu\text{-OR})(\mathrm{cod})]_2 + n\mathrm{PR}_3$.

Experimental

The reactions were carried out at room temperature under nitrogen by standard Schlenk techniques. $[\mathrm{Ir}(\mu\text{-OMe})(\mathrm{cod})]_2$ [15], $[\mathrm{Rh}(\mu\text{-OMe})(\mathrm{cod})]_2$ [15], $\mathrm{Ir(C{\equiv}CPh)(CO)(PCy_3)}$ [8] were prepared as previously reported. ^{1}H NMR spectra were recorded with $\mathrm{CDCl_3}$ solutions at room temperature on a Varian XL 200 spectrometer. IR spectra were recorded on a Perkin–Elmer 783 spectrophotometer. Elemental analyses were carried out with a Perkin–Elmer 240C elemental analyzer.

Preparation of $\mathrm{Rh(C{\equiv}CPh)(cod)(PCy_3)}$

A mixture of $[\mathrm{Rh}(\mu\text{-OMe})(\mathrm{cod})]_2$ (100 mg, 0.20 mmol), $\mathrm{PCy_3}$ (116 mg, 0.41 mmol) and PhC≡CH (90 μl, 0.80 mmol) in diethyl ether (15 ml) was stirred for 30 min. The yellow solution was concentrated under reduced pressure and methanol (10 ml) was added. The yellow precipitate was filtered off, washed with methanol, and dried under vacuum. Yield 86 mg (78%). Anal. Found: C, 68.1; H, 8.1.

$C_{34}H_{50}PRh$ calcd.: C, 68.9; H, 8.5%, IR (Nujol): ν(C≡C) 2081 cm^{-1}. ^{1}H NMR ($CDCl_3$, ppm): δ 1.1–2.3(m, 41h, C_6H_{11}, CH_2), δ 4.16(br, 2H, =CH), δ 5.34 (br, 2H, =CH), δ 6.7–7.4(m, 5H, C_6H_5).

Preparation of Ir(C≡CPh)(cod)(PPh$_3$)$_2$

A mixture of [Ir(μ-OMe)(cod)]$_2$ (100 mg, 0.15 mmol), PPh_3 (160 mg, 0.61 mmol) and PhC≡CH (66 μl, 0.60 mmol) in diethyl ether (15 ml) was stirred for 30 min. The solution was concentrated under reduced pressure and methanol (10 ml) was added. The white precipitate formed was filtered off, washed with methanol, and dried under vacuum. Yield 210 mg (75%). Anal. Found: C, 67.8; H, 5.3. $C_{52}H_{47}IrP_2$ calcd.: C, 67.5, H, 5.1%. IR (Nujol): ν(C≡C) 2106 cm^{-1}. ^{1}H NMR ($CDCl_3$, ppm): δ 1.78(br, 8H, CH_2), δ 3.65(br, 4H, =CH), δ 6.6–7.7(m, 35H, C_6H_5).

Preparation of Ir(C≡CPh)(cod)(dppe)

The ligand dppe (36 mg, 0.09 mmol) was added to a solution of Ir(C≡CPh)(cod)(PCy_3) (60 mg, 0.09 mmol) in diethyl ether (20 ml), and the mixture was stirred for 3 h. The white precipitate formed was filtered off, washed with diethyl ether, and dried under vacuum. Yield 52 mg (74%). Anal. Found: C, 62.8; H, 5.5. $C_{42}H_{41}IrP_2$ calcd.: C, 63.0; H, 5.2%. IR (Nujol): ν(C≡C) 2105 cm^{-1}.

Preparation of Ir(C≡CPh)(CO)(PCy$_3$)$_2$

Carbon monoxide was bubbled through a solution of Ir(C≡CPh)(cod)(PCy_3) (60 mg, 0.09 mmol) and PCy_3 (25 mg, 0.09 mmol) in diethyl ether (20 ml) for 1 h. Addition of methanol produced a yellow precipitate, which was filtered off, washed with methanol, and dried under vacuum. Yield 50 mg (64%). Anal. Found: C, 61.3; H, 8.1. $C_{45}H_{71}IrOP_2$ calcd.: C, 61.2; H, 8.1% IR (CH_2Cl_2): ν(C≡C) 2095 cm^{-1}, ν(C≡O) 1926 cm^{-1}.

Preparation of Rh(C≡CPh)(CO)(PCy$_3$)$_2$

This complex was prepared by the procedure described for Ir(C≡CPh)(CO)(PCy_3)$_2$ from Rh(C≡CPh)(cod)(PCy_3) (80 mg, 0.13 mmol) and PCy_3 (38 mg, 0.13 mmol). The yield of the yellow Rh(C≡CPh)(CO)(PCy_3)$_2$ complex was 56 mg (52%). Anal. Found: C, 67.7; H, 8.7. $C_{45}H_{71}OP_2Rh$ calcd.: C, 68.2; H, 9.0% IR (CH_2Cl_2): ν(C≡C) 2090 cm^{-1}, ν(C≡O) 1940 cm^{-1}.

Preparation of Ir(C≡CPh)(CO)$_2$(dppe)

Carbon monoxide was bubbled through a suspension of Ir(C≡CPh)(cod)(dppe) (150 mg, 0.18 mmol) in dichloromethane (20 ml) for 1 h. Addition of diethyl ether (15 ml) produced a pale yellow precipitate, which was filtered off, washed with diethyl ether, and dried under vacuum. Yield 81 mg (56%). Anal. Found: C, 57.9; H, 3.7. $C_{36}H_{29}IrO_2P_2$ calcd.: C, 57.8; H, 3.9%. IR (CH_2Cl_2): ν(C≡C) 2115 cm^{-1}, ν(C≡O) 1990, 1940 cm^{-1}.

Preparation of IrH$_2$(C≡CPh)(CO)(dppe)

Hydrogen was bubbled through a solution of Ir(C≡CPh)(CO)$_2$(dppe) (70 mg, 0.09 mmol) in dichloromethane (20 ml) for 90 min. The resulting yellow solution was concentrated under reduced pressure and methanol (10 ml) was added. The white precipitate formed was filtered off, washed with methanol, and dried under vacuum. Yield 35 mg (52%). Anal. Found: C, 57.8; H, 3.9. $C_{35}H_{31}IrOP_2$ calcd.: C, 58.2; H, 4.3%. IR (CH_2Cl_2): $\nu(C{\equiv}C)$ 2120 cm^{-1}, $\nu(Ir{-}H)$ 2100 cm^{-1}, $\nu(C{\equiv}O)$ 2002 cm^{-1}. ^1H NMR ($CDCl_3$, ppm): δ −10.37(t, J(H–P) 19.0 Hz, IrH), δ −9.6(dd, J(H–P) 137.8, 13.3 Hz, IrH), δ 2.2–2.9(m, 4H, CH_2), δ 7.2–7.9(m, 25H, C_6H_5).

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