Cycloheptatrienyl-bridged heterobimetallic complexes: synthesis and reactivity of $(\mu\text{-}C_7H_7)\overline{Fe(CO)_3Ir}(CO)_2$

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Abstract

The synthesis and spectroscopic properties of the cycloheptatrienyl-bridged iron-iridium complexes $(\mu\text{-}C_7H_7)\overline{Fe(CO)_3Ir}(CO)_2$ and $(\mu\text{-}C_7H_7)\overline{Fe(CO)_3Ir}(CO)(PPh_3)$ are described.

The chemistry of heterobimetallic transition-metal complexes is of current interest [1]. Owing to its flexible bonding capability the cycloheptatrienyl ligand has become a versatile building block for the synthesis of polyolefin-bridged heterobimetallic complexes. Some time ago we have described the preparation of $(\mu\text{-}C_7H_7)\overline{Fe(CO)_3Rh}(CO)_2$ (2) and more recently a detailed spectroscopic and reactivity study of this compound has been published [3]. In a continuation of these investigations we now describe the preparation and characterization of some μ-cycloheptatrienylironiridium complexes.

Starting with $Na[(C_7H_7)Fe(CO)_3]$ [4] the direct route to $(\mu\text{-}C_7H_7)\overline{Fe(CO)_3Ir}(CO)_2$ (1) was complicated by the non-availability of "$[Ir(CO)_2Cl]_2$". It was found, however, that $Na[(C_7H_7)Fe(CO)_3]$ reacts with commercially available $[Ir(CO)_3Cl]_x$ to give complex 1 in low yields (7%) together with considerable amounts of the known dimer $[(C_7H_7)Fe(CO)_3]_2$ [5]. A slight improvement of the yield (average of several runs, 17%) was achieved by using an activated form of $[Ir(CO)_3Cl]_x$, which was obtained by in situ carbonylation of $[Ir(COE)_2Cl]_2$ (COE = cyclooctene). Another obvious route to $(\mu\text{-}C_7H_7)\overline{Fe(CO)_3Ir}(CO)_2$ (1) was found to be no less disappointing. Although $(\mu\text{-}C_7H_7)\overline{Fe(CO)_3Ir}(COD)$ (2) [6] does react with CO in virtually quantitative fashion to give 1, the yield of the former compound, in our hands, was at best the same as that of 1 obtained in one step from the activated carbonyliridium precursor. The carbonylation of 2, requiring heat at 100°C, proved much more difficult than that of the analogous Fe–Rh complex which occurred readily at room temperature [3]. Even though this trend is consistent with the greater metal–ligand bond strengths in the iridium complex [7], the remarkable

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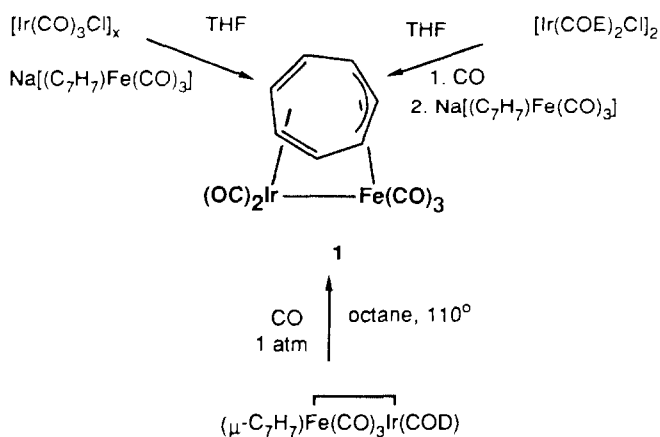
Scheme 1

difference in reactivity was unexpected. Scheme 1 summarizes the different routes to **1**.

After recrystallization from hexane complex **1** forms orange-brown needles. As expected, the ^{1}H and ^{13}C NMR data indicate rapid rotation of the bridging cycloheptatrienyl ligand. The slow exchange limiting spectrum was not obtained even at $-78°$C. Rapid ring whizzing is typical for cisoid bimetallic μ-cyclopolyolefin complexes [2,6]. The variable-temperature ^{13}C NMR spectra of **2** indicate that the COD ligand is also involved in a fluxional process (Fig. 1). At room temperature the spectrum shows two singlets for the aliphatic carbon atoms (C_a) and two singlets in the olefinic region (C_o). Fast exchange is observed at $+80°$C. From the coalescence temperature ($+60°$C) the value of the free energy of activation for COD rotation is calculated to be 15.7 kcal/mol [8]. This is significantly greater than the rotational barrier in the analogous Fe–Rh compound, 11.6 kcal/mol [3], and again reflects the greater metal-to-COD bond strengths in the iridium derivative.

Although the carbonylation experiments had revealed that the iron-iridium-cyclooctadiene system is significantly less reactive than the corresponding iron-rhodium derivative, the fully carbonylated complex **1** was found to undergo a clean and facile phosphine substitution reaction. Treatment of **1** with PPh_3 at room temperature gave red, crystalline $(\mu\text{-}C_7H_7)FeIr(CO)_4(PPh_3)$ (**3**) in 81% yield. As with the analogous rhodium derivative, $(\mu\text{-}C_7H_7)FeRh(CO)_4(PPh_3)$ [3], the infrared spectrum of **3** indicates the presence of both all-terminal, **3a**, and carbonyl-bridged, **3b**, isomers. The latter involves a change of the bonding mode of the $\mu\text{-}C_7H_7$ moiety

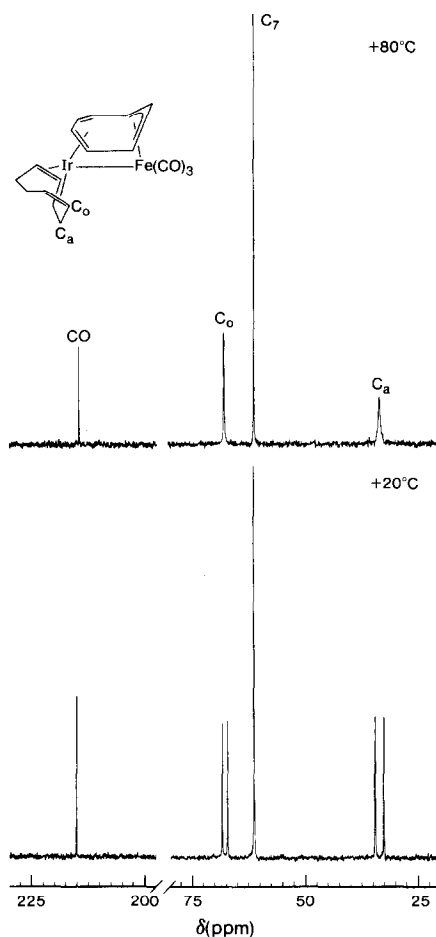**3a**

3b
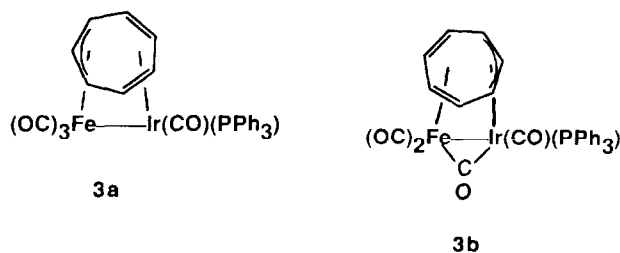
Fig. 1. Variable temperature ^{13}C NMR spectra of (μ-C$_7$H$_7$)Fe(CO)$_3$Ir(COD) (2).

from η^3-Fe,η^4-Ir to η^4-Fe,η^3-Ir. Although clearly seen in the infrared spectrum, the interconversion between 3a and 3b must be very rapid since even at $-75\,^\circ$C, no bridging carbonyl signal could be seen in the ^{13}C NMR spectrum of 3 (Fig. 2). The observation of a sharp singlet for the Fe(CO)$_3$ moiety indicates that scrambling of the carbonyl ligands on iron is still rapid at this temperature. The doublet appearance of the carbonyl group on iridium, due to ^{31}P–^{13}C coupling, clearly establishes that phosphines substitution occurs exclusively at the iridium center.

As the temperature is raised the signals due to the carbonyl groups broaden indicating the onset of intermetallic exchange of CO ligands. The process is fast at $+95\,^\circ$C and gives rise to a single, time averaged carbonyl signal. The free energy of activation, calculated at the coalescence temperature [9] is 10.8 kcal/mol ($T_c \approx 20\,^\circ$C). It is somewhat surprising that this value is lower than that found (15.4 kcal/mol [3]) in the analogous iron-rhodium derivative. Although the observation that carbonyl group migration is faster between Fe–Ir than Fe–Rh is contrary to the well known greater reluctance of 3rd row transition metals to support bridging carbonyl groups, it should be pointed out that so far only a few systematic triad
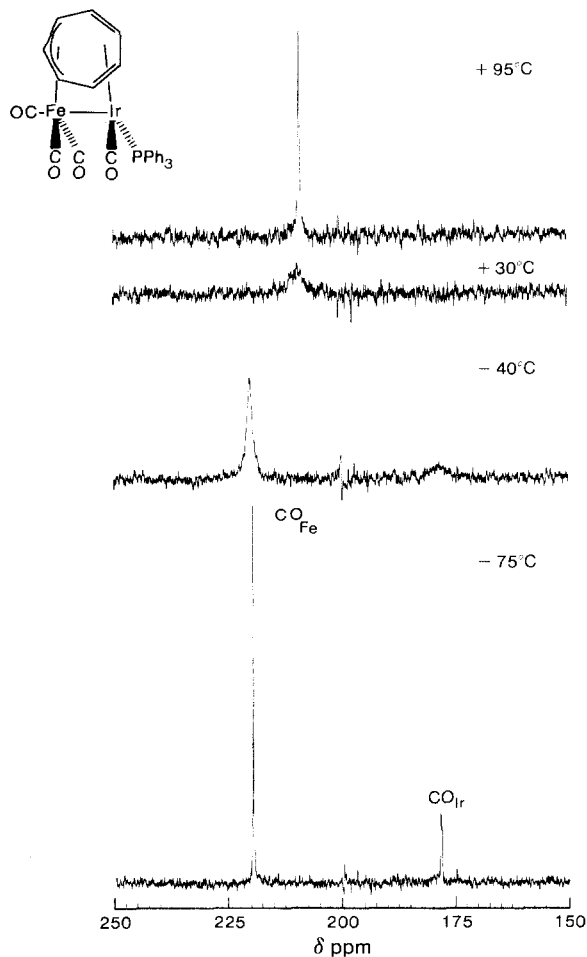
Fig. 2. Variable temperature ^{13}C NMR spectra of $(\mu\text{-}C_7H_7)\overline{Fe(CO_3}Ir(CO)(PPh_3)$ (3).

comparisons of this behavior have been carried out in binuclear complexes and at least in one case the difference between first and second row metals is small and the relative order is dependent on the ancillary ligands [10*]. Clearly further comparison with different metal combinations will have to be carried out before it can be concluded that in cycloheptatrienyl-bridged heterobimetallic complexes the activation energy for global carbonyl group exchange, as a rule, decreases as the metal triad is descended.

Experimental

All reactions were carried out under purified nitrogen using standard Schlenk techniques and carefully dried solvents. Na[(C$_7$H$_7$)Fe(CO)$_3$] [4], [Ir(COD)Cl]$_2$ [11] and [Ir(COE)$_2$Cl]$_2$ [12] were prepared according to literature methods. IR spectra:

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* A reference number with an asterisk indicates a note in the list of references.

Nicolet MX-1. Mass spectra: A.E.I. MS-12 spectrometer. NMR spectra: Bruker WP-200 or Bruker WP-400.

μ-(η-Cycloheptatrienyl)dicarbonyliridiumtricarbonyliron(Fe–Ir) (1)

Method (a): Na[(C$_7$H$_7$)Fe(CO)$_3$] (2.0 g, 7.9 mmol) in THF (30 ml) was added to a suspension of [Ir(CO)$_3$Cl]$_x$ (3.0 g, 9.6 mmol) in THF (50 ml) and the mixture was stirred for 3 h at 40°C. After evaporation to dryness the brown residue was extracted with warm toluene (2 × 20 ml) and the combined extracts were chromatographed on a hexane-packed silica gel column (3 × 20 cm). Yellow [(C$_7$H$_7$)Fe(CO)$_3$]$_2$ was separated by elution with hexane. Changing the solvent to toluene/hexane (1/1) produced a large orange band of the product. Removal of the solvent followed by recrystallisation from hexane (15 ml) gave orange-brown needles of **1** (0.25 g, 7%), m.p. 131–132°C.

Method (b): [Ir(COE)$_2$Cl]$_2$ (2.00 g, 2.23 mmol) in THF (180 ml) was converted into activated [Ir(CO)$_3$Cl]$_x$ by passing a rapid stream of CO through the solution for 5 min. To the resulting black suspension Na[(C$_7$H$_7$)Fe(CO)$_3$] (1.28 g, 5.06 mmol, slight excess) in THF (60 ml) was added slowly, dropwise over a period of 7.5 h. The resulting red-brown reaction mixture was extracted with toluene (2 × 15 ml) and the combined extracts were twice chromatographed as described under (a). Yield 0.374 g (17%). The reaction is unpredictable and variable yields were obtained, minimum of 10% and maximum of 25%.

Method (c): 25 mg of (μ-C$_7$H$_7$)Fe(CO)$_3$Ir(COD) (**2**) was dissolved in octane (10 ml). The solution was heated to 110°C while maintaining a slow stream of CO through the solution. After 0.5 h complete conversion to the pentacarbonyl **1** occurred as judged by IR spectroscopy. Anal. Found: C, 29.73; H, 1.76. C$_{12}$H$_7$FeIrO$_5$ calcd.: C, 30.08; H, 1.47%. IR (hexane): ν(CO) 2057vs, 2011vs, 1996vs, 1966s cm^{-1}. MS (70 eV): m/e 480 (M^+, 24.5%), 452 ($M^+ -$ CO, 18.7), 424 ($M^+ -$ 2CO, 18.9), 396 ($M^+ -$ 3CO, 38.9), 368 ($M^+ -$ 4CO, 100), 340 ($M^+ -$ 5CO, 57.1), 260 ((C$_7$H$_7$)Fe(CO)$_3{}^+$, 25.1), 91 (C$_7$H$_7{}^+$, 15.5). ^{1}H NMR (CDCl$_3$): δ 4.06 (s, C$_7$H$_7$) ppm. ^{13}C NMR(CD$_2$Cl$_2$): δ 214.9 (FeCO), 174.6 (IrCO), 60.6 (C$_7$H$_7$) ppm.

μ-(η-Cycloheptatrienyl)tricarbonylironcyclooctadieneiridium(Fe–Ir) (2) [6] from Na[(C$_7$H$_7$)Fe(CO)$_3$]

Na[(C$_7$H$_7$)Fe(CO)$_3$] (2.3 g, 9.1 mmol) in THF (30 ml) was reacted with [Ir(COD)Cl]$_2$ (3.0 g, 4.5 mmol) in THF (30 ml) for 2 h at room temperature. After removal of the solvent the crude product was chromatographed on silica gel column (3 × 10 cm). **2** was eluted with toluene as a dark red-brown band. Recrystallization from hexane (100 ml) gave analytically pure **2** (0.69 g, 15%) as black crystals, m.p. 147°C. IR and NMR data were in good agreement with the literature values. MS (70 eV): m/e 532 (M^+, 20.7%), 504 ($M^+ -$ CO, 17.9), 476 ($M^+ -$ 2CO, 32.5), 448 ($M^+ -$ 3CO, 58.9), 91 (C$_7$H$_7{}^+$, 47.1).

μ-(η-Cycloheptatrienyl)tricarbonyliron-carbonyl(triphenylphosphine)iridium(Fe–Ir) (3)

Triphenylphosphine (50 mg, 0.2 mmol) in hexane (10 ml) was added to (μ-C$_7$H$_7$)Fe(CO)$_3$Ir(CO)$_2$ (**1**) (80 mg, 0.2 mmol) in hexane (10 ml) and the mixture was stirred for 10 min. The resulting red precipitate was washed with 5 ml of pentane and dried to give red microcrystals of **3** (95 mg, 81%), m.p. 165°C. Anal. Found: C, 48.35; H, 3.19. C$_{29}$H$_{22}$FeIrO$_4$P calcd.: C, 48.82; H, 3.11%. IR (CH$_2$Cl$_2$):

ν(CO) 2009m, 1996m, 1961s, 1936m, 1910sh, 1767w,br cm^{-1}. MS (70 ev): m/e 714 (M^+, 0.9%), 630 ($M^+ - 3CO$, 17.9), 602 ($M^+ - 4CO$, 0.9), 262 (PPh$_3^+$, 41.6), 91 (C$_7$H$_7^+$, 39.6). ^{1}H NMR (CD$_2$Cl$_2$): δ 7.56–7.40 (m, 15H, C$_6$H$_5$), 3.82 (s, 7H, C$_7$H$_7$). ^{13}C NMR (toluene-d_8) -75°C: δ 219.8 (s, FeCO), 178.9 (d, IrCO, J(P–C) 10.4 Hz), 60.2 (s, C$_7$H$_7$) ppm; $+95$°C: δ 209.2 (s, averaged FeCO and IrCO), 60.5 (s, C$_7$H$_7$) ppm. ^{31}P NMR (CD$_2$Cl$_2$): δ 3.50 (s, PPh$_3$) ppm.

Acknowledgements

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