Synthesis, Fluxional Behaviour and X-Ray Crystal Structure of $[Fe(CO)_3(\mu\text{-}\eta^3:\eta^2\text{-}C_7H_7)Pd(\eta^5\text{-}C_5H_5)]$

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Reaction of $K[(\eta^3\text{-}C_7H_7)Fe(CO)_3]$ with $[(1,5\text{-}\eta^4\text{-}C_8H_{12})Pd(\eta^5\text{-}C_5H_5)]BF_4$ gives the title compound which is the first case of a bridging cycloheptatrienyl metal–metal bonded complex having an uncoordinated double bond in the ring and detectable low-temperature limiting ^1H and ^{13}C NMR spectra.

Several transition metal–metal bonded complexes having a bridging cycloheptatrienyl moiety have been reported recently.[1,2] Common features in these complexes are the coordination of the metal–metal unit to all the carbon atoms of the ring and the high degree of fluxional behaviour.[3] Indeed attempts to determine the slow-exchange limiting NMR spectrum of the C_7H_7 ring have failed, except for a complex with a hydrogen bridge between two metal units.[4]

In this communication we report the synthesis of $[Fe(CO)_3(\mu\text{-}\eta^3:\eta^2\text{-}C_7H_7)Pd(\eta^5\text{-}C_5H_5)]$, the first example of a cycloheptatrienyl bridged bimetallic complex having an uncoordinated double bond of the ring and showing low-temperature limiting ^1H and ^{13}C NMR spectra. A likely precursor for the synthesis of cycloheptatrienyl bridged heterobimetallic complexes is $[(\eta^3\text{-}C_7H_7)Fe(CO)_3]^-$,[5] a bifunctional nucleophile where both ring carbons[6] and the iron centre[7] can be subject to electrophilic attack. Reaction of $[(\eta^3\text{-}C_7H_7)Fe(CO)_3]^-$ with $[(1,5\text{-}\eta^4\text{-}C_8H_{12})Pd(\eta^5\text{-}C_5H_5)]^+$[7] at −78 °C in tetrahydrofuran (THF), evaporation of solvent, extraction with hexane, and crystallization affords brown crystals of **1** according to reaction (1). Its crystal structure has been determined.

$$K[(\eta^3\text{-}C_7H_7)Fe(CO)_3] + [(1,5\text{-}\eta^4\text{-}C_8H_{12})Pd(\eta^5\text{-}C_5H_5)]BF_4 \xrightarrow[\text{THF}]{}$$

$$\rightarrow [Fe(CO)_3(\mu\text{-}\eta^3:\eta^2\text{-}C_7H_7)Pd(\eta^5\text{-}C_5H_5)] + KBF_4 + 1,5\text{-}C_8H_{12} \qquad (1)$$

1, 30% yield

The title compound consists of a heterobimetallic unit, with an Fe–Pd bond distance [2.653(1) Å] slightly longer than those found in $[Fe_4Pd(CO)_{16}]^{2-}$ (average 2.599 Å),[8] bridged by a cycloheptatrienyl group in the 'unique' ($\mu\text{-}\eta^3:\eta^2$) coordination mode (Fig. 1).† The π electrons of the C_7H_7 moiety are partially localized into one 'allylic' and two 'ethylenic' moieties separated by 'single' bonds (av. 1.444 Å); it is noteworthy that one of the two double bonds [C(4)–C(10), the shortest] is uncoordinated [Pd–C(4) 2.982 Å; Pd–C(10) 3.552 Å]. The Fe environment is close to that found in $[Fe(CO)_3(\mu\text{-}\eta^3:\eta^4\text{-}C_7H_7)Rh(CO)_2]$,[9] while the 'three-coordination' around the Pd atom resembles that in the $[Pd(\eta^5\text{-}$

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† *Crystal data* for **1**: $C_{15}H_{12}FeO_3Pd$; M = 402.51, monoclinic, space group $P2_1/n$ (non standard setting of $P2_1/c$, No. 14), a = 8.772(2), b = 10.308(6), c = 16.078(3) Å, β = 93.38(2)°, U = 1451(1) Å^3, $F(000)$ = 792, Z = 4, D_c = 1.84 g cm^{-3}, Mo-Kα radiation, λ = 0.71073 Å, μ(Mo-Kα) = 22.2 cm^{-1}. Intensities were measured with a CAD4 automatic diffractometer at room temperature with θ ranging from 3 to 25°; data were corrected for absorption (max–min relative transmission factors 1.00–0.75), Lorentz-polarization effects and decay (3%). 1929 reflections with $I > 3\sigma(I)$ were used in the structure refinements. The hydrogen atoms were located from a Fourier difference map and refined. The final R value was 0.019 (R_w = 0.024).

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

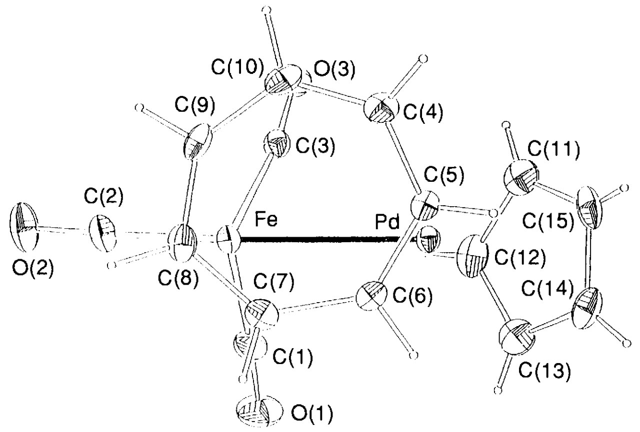

Fig. 1 ORTEP drawing (30% probability ellipsoids) of [Fe(CO)$_3$(μ-η^3:η^2-C$_7$H$_7$)Pd(η^5-C$_5$H$_5$)]. Selected bond lengths (Å) with standard deviations in parentheses are: Pd–Fe 2.653(1), Pd–C(5) 2.153(3), Pd–C(6) 2.150(3), Pd–C(11) 2.277(4), Pd–C(12) 2.274(4), Pd–C(13) 2.427(4), Pd–C(14) 2.434(4), Pd–C(15) 2.320(4), Fe–C(1) 1.795(4), Fe–C(2) 1.770(4), Fe–C(3) 1.794(4), Fe–C(7) 2.172(3), Fe–C(8) 2.058(3), Fe–C(9) 2.194(3), C(4)–C(5) 1.438(5), C(4)–C(10) 1.331(5), C(5)–C(6) 1.406(5), C(6)–C(7) 1.443(5), C(7)–C(8) 1.393(5), C(8)–C(9) 1.415(5), C(9)–C(10) 1.452(5).

C$_5$H$_5$)(PEt$_3$)(styrene)]$^+$ cation.[10] The Pd–C$_5$H$_5$ interactions *trans* to the η^2-bonded C atoms are significantly shorter than the others (2.275 *vs.* 2.394 Å), analogous to the aforementioned cation.

Both metals follow formally the 18 electrons rule; indeed coordination of the η^5-cyclopentadienyl unit allows linkage of palladium to only one 'ethylenic' moiety of the C$_7$H$_7$ ring.

The room temperature ^{1}H NMR spectrum [two signals at δ 5.9 (5H, C$_5$H$_5$) and 4.72 (7H, C$_7$H$_7$)] is consistent with a fluxional behaviour of **1** in solution. Similarly the ^{13}C{^{1}H} NMR spectrum of **1** gives a singlet for C$_5$H$_5$ at δ 101.6 and a singlet for C$_7$H$_7$ at δ 82.2. As the temperature is lowered, the single, sharp, time-averaged signal of the C$_7$H$_7$ ring (in both ^{1}H and ^{13}C NMR spectra) broadens, disappears and finally reemerges as seven signals, consistent with the ground state structure of complex **1**. Therefore the presence of an uncoordinated C–C double bond increases the activation energy of ring rotation.

Analysis of the variable temperature ^{13}C NMR spectra shows that carbonyl exchange at iron also occurs, this process being independent of ring rotation.

The synthesis of the title compound is based on the lability of 1,5-C$_8$H$_{12}$ in [(1,5-η^4-C$_8$H$_{12}$)Pd(η^5-C$_5$H$_5$)]$^+$. This interesting characteristic is displayed by other cationic [(1,5-η^4-C$_8$H$_{12}$)PdL]$^+$ complexes. When L = η^3-C$_3$H$_5$, good yields of [Fe(CO)$_3$(μ-η^3:η^4-C$_7$H$_7$)Pd(η^3-C$_3$H$_5$)][2] have been obtained. Further studies to prove the utility of [(η^4-C$_8$H$_{12}$)PdL]$^+$ as PdL$^+$ transfer to polyalkenic units are in progress.

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