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Preliminary Communication

A stable dicarbonyl(cycloocta-1,5-diene)(η^1-indenyl)iridium intermediate in the substitution reaction of cycloocta-1,5-diene(η^5-indenyl)iridium with carbon monoxide *

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Abstract

Stable dicarbonyl(cycloocta-1,5-diene)(η^1-indenyl)iridium is formed by addition of CO to cyclooctadiene(η^5-indenyl)iridium in CD_2Cl_2 at low temperature. On raising the temperature above 250 K, the η^1 species changes quantitatively into dicarbonyl(η^5-indenyl)iridium.

Associative ligand substitution reactions in cyclopentadienyl (Cp) and indenyl transition metal complexes are believed to occur through an $\eta^5 \rightarrow \eta^3 \rightarrow \eta^5$ mechanism [1]. Indenyl metal complexes are far more reactive than the corresponding Cp analogues, and this enhanced reactivity has been attributed to an easier "ring slippage" towards an η^3 (or even η^1) intermediate favoured by the aromatization of the fused benzene ring ("indenyl effect" [2]). However, to our knowledge, direct evidence of these intermediates is elusive [3], even if their postulation is in some cases necessary to explain the reaction products [3,4].

In this communication we report direct evidence for the formation of an η^1 species as an intermediate in the associative substitution reaction of [Ir(η^5-indenyl)(COD)] (COD = cycloocta-1,5-diene) with carbon monoxide.

Bubbling CO through a CD_2Cl_2 solution of [Ir(η^5-indenyl)(COD)] * at room temperature leads to its quantitative conversion to [Ir(η^5-indenyl)$(CO)_2$] ** within a few minutes [4]. In contrast, by carrying out the reaction at or below 243 K, the complex is quantitatively transformed into a stable species within 1 h. The ^1H NMR spectrum of this species is shown in Fig. 1 ***.

The ^{13}C spectrum suggests that two CO molecules (δ 176.89 and 176.77 ppm) have been added to the metal. In addition, the ABCDEFG pattern shown by the ^1H NMR spectrum of the indenyl moiety, together with the magnetic nonequivalence of all the carbon atoms, indicates unambigously that this ligand is bonded to Ir in an η^1 mode. In particular, the resonance attributed to H(1) is found at 3.61 δ. The signals of olefinic protons of COD appear as two distinct multiplets (due to the chiral nature of the η^1-indene) at *ca.* 4.0 and 4.2 δ at 233 K and they are broader than the other signals in the spectrum (see Fig. 1). As the

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* [Ir(η^5-indenyl)(COD)]: solvent, CD_2Cl_2; 298 K, δ in ppm from internal Me_4Si; ^1H NMR data (ν_0 400.13 MHz, spectral parameters obtained by computer simulation): δ 7.270 and 7.095 (2H each, AA′BB′ system, H(4,7) and H(5,6), respectively), 5.971 (1H H(2)), 5.319 (2H, H(1,3)), 3.87 (4H, m, olefinic COD protons), and 1.7-1.5 (8H, m, aliphatic COD protons). Proton–proton coupling constants: $^3J_{1,2} = {}^3J_{2,3}$ 2.55, $^4J_{1,3}$ 2.52, $^5J_{1,4} = {}^5J_{3,7}$, 1.18, $^4J_{1,7} = {}^4J_{3,4}$ −0.54, $^3J_{4,5} = {}^3J_{6,7}$ 8.31, $^4J_{4,6} = {}^4J_{5,7}$ 1.02, $^5J_{4,7}$ 0.97, and $^3J_{1,2}$ 6.81 Hz. ^{13}C data (ν_0 100.61 MHz) δ 123.81 ($C_{5,6}$), 120.90 ($C_{4,7}$), 113.61 ($C_{3a,7a}$), 84.35 (C_2), 71.95 ($C_{1,3}$), 50.41 (=C–H in C_8H_{12}), and 33.21 (–CH_2 in C_8H_{12}).

** [Ir(η^5-indenyl)$(CO)_2$]: ^1H NMR data (CD_2Cl_2; 298 K): δ 7.381 and 7.245 (2H each, AA′BB′ system, H(4,7) and H(5,6), respectively), 6.179 (1H, H(2)), and 5.836 (2H, H(1,3)). Proton–proton coupling constants: $^3J_{1,2} = {}^3J_{2,3}$ 2.82, $^4J_{1,3}$ 2.83, $^5J_{1,4} = {}^5J_{3,7}$ 1.03, $^4J_{1,7} = {}^4J_{3,4}$ −0.24, $^3J_{4,5} = {}^3J_{6,7}$ 8.27, $^4J_{4,6} = {}^4J_{5,7}$ 0.99, $^5J_{4,7}$ 0.95, and $^3J_{1,2}$ 6.98 Hz. ^{13}C data: δ 172.72 (C≡O), 126.63 ($C_{5,6}$), 120.56 ($C_{4,7}$), 115.88 ($C_{3a,7a}$), 94.35 (C_2), 72.17 ($C_{1,3}$).

*** [Ir(η^1-indenyl)$(CO)_2$(COD)]: ^1H NMR data (CD_2Cl_2; 233 K (assignments obtained by {^1H}–^1H NOE measurements): 7.565 (1H, m, H_7), 7.336 (1H, m, H_4), 7.116 (1H, m, H_6). 7.086 (1H, m, H_5), 6.782 (1H, m, H_2), 6.449 (1H, m, H_3), 4.12 and 3.96 (two broad m, 2H, each, =CH COD protons), 2.7–2.3 ppm (8 H, broad m, CH_2 protons), and 3.610 (1H, m, H_1). Proton–proton coupling constants: $^3J_{1,2}$ 1.80, $^4J_{1,3}$ 1.01, $^4J_{1,7}$ 0.84, $^3J_{2,3}$ 5.15, $^5J_{3,7}$ 1.02. $^3J_{4,5}$ 7.58, $^4J_{4,6}$ 1.19. $^5J_{4,7}$ 0.53, $^3J_{5,6}$ 7.31, $^4J_{5,7}$ 1.15, and $^3J_{6,7}$ 7.69 Hz. ^{13}C NMR data (CD_2Cl_2: 233 K; assignments obtained by selective proton decoupling): 176.89 and 176.77 (1C each, C≡O), 156.83 and 141.99 (C_{3a} and C_{7a}), 150.16 (C_2), 124.37 (C_6), 124.09 (C_7), 123.35 (C_5), 121.98 (C_3), 120.80 (C_4), *ca.* 76 (very broad, =C–H in C_8H_{12}), 35.07 and 33.62 (2C each, broad, –CH_2 in C_8H_{12}), and 20.50 (C_1).

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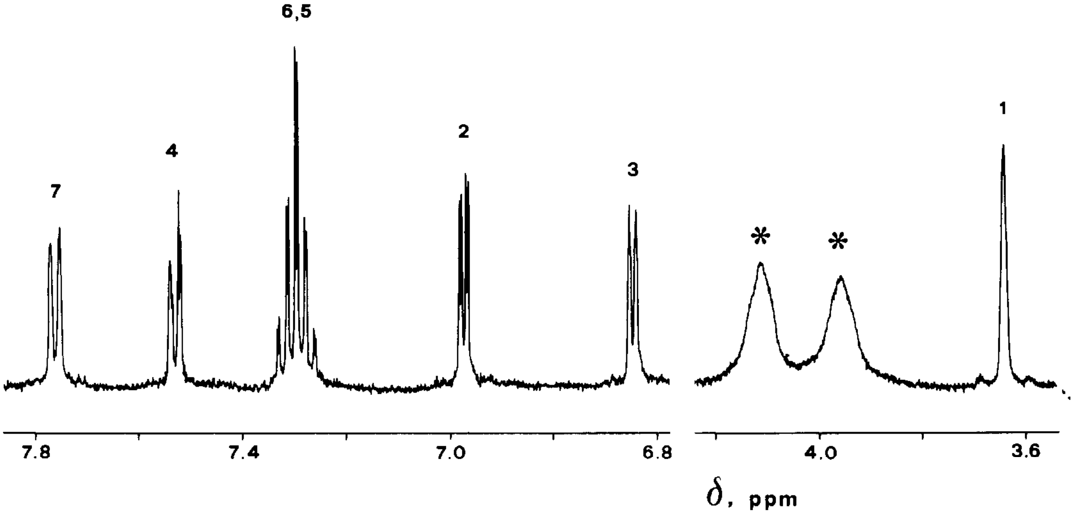

Fig. 1. ^{1}H NMR spectrum of [Ir(η^1-indenyl)(CO)$_2$(COD)]. Solvent, CD_2Cl_2; 243 K; ν_0 400.133 MHz. For proton labelling, see Fig. 2. The asterisks indicate the resonances of the olefinic hydrogen atoms of COD. The resonances attributed to the methylene protons of COD are omitted.

temperature is lowered, they further broaden, disappear (at *ca.* 203 K), and finally reemerge as four signals (δ 4.93, 4.87, 3.46, and 3.18) at 173 K. For this fluxional process $\Delta G^{\ddagger}$ was calculated to be 8.4 ± 0.5 Kcal mol^{-1}. The resonances due to the corresponding ^{13}C nuclei behave similarly, since they appear as a very broad signal (δ *ca.* 76 ppm) at 233 K, and as four singlets (δ 92.17, 92.12, 59.80, and 59.26) at 173 K. Thus, COD undergoes an intramolecular exchange between two nonequivalent coordination sites. If the addition product has a bipyramidal trigonal structure as shown in Fig. 3, the fluxional process would involve one axial

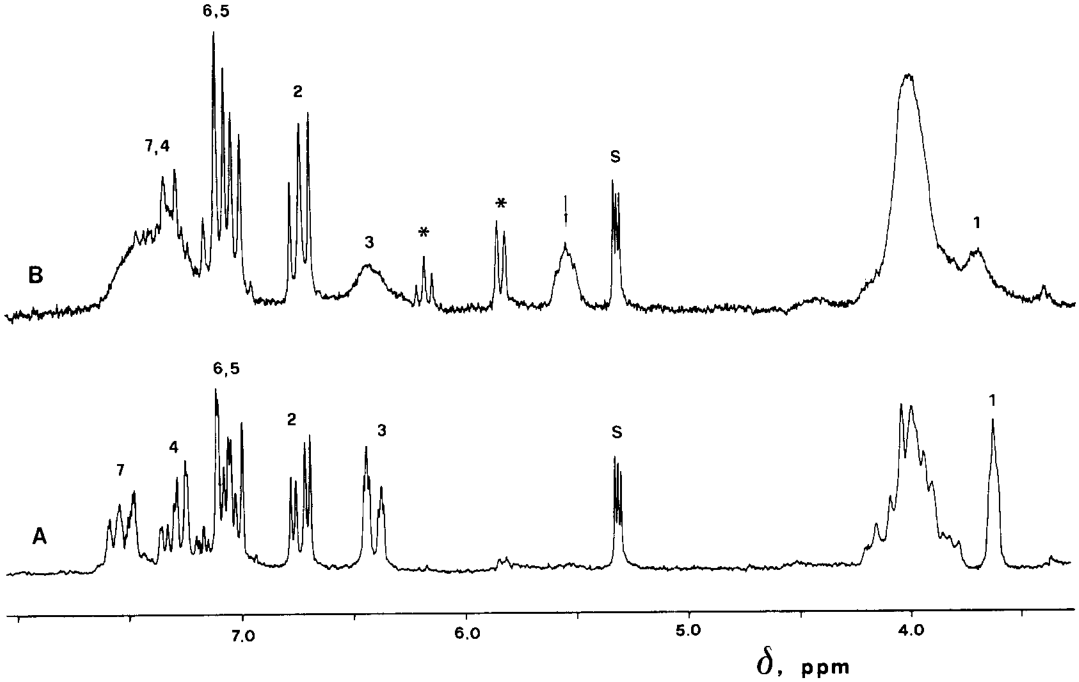

Fig. 2. Temperature dependence of the ^{1}H NMR spectrum of [Ir(η^1-indenyl)(CO)$_2$(COD)] at ν_0 80.13 MHz. For proton labelling, see Fig. 2. Solvent, CD_2Cl_2; S indicates solvent signals. A: 243 K. B: 270 K; the asterisks and the arrow indicate some signals of [Ir(η^5-indenyl)(CO)$_2$] and uncoordinated COD, respectively.

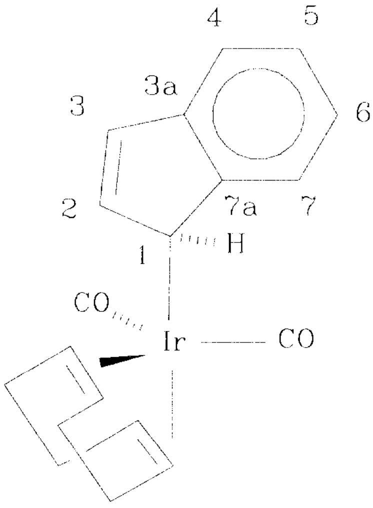

Fig. 3.

and one equatorial coordination position for the double bonds of the olefin.

On raising the temperature above 250 K, the η^1 species converts quantitatively into the substitution product, [Ir(η^5-indenyl)(CO)$_2$], with first-order kinetics. The process was monitored by ^{1}H NMR spectroscopy at four different temperatures, and from the values of the rate constants, 10^4k (T/K): 0.591 ± 0.006 (253); 1.23 ± 0.02 (258); 2.24 ± 0.02 (263); 7.01 ± 0.06 (270), the activation parameters $\Delta H^{\ddagger} = 18.8 \pm 0.5$ Kcal mol^{-1} and $\Delta S^{\ddagger} = -3.4 \pm 2.0$ cal mol^{-1} K^{-1} were calculated.

Thus, the $\eta^1 \rightarrow \eta^5$ change of iridium hapticity which involves the loss of the two π bonds with COD and restoration of the aromaticity of the Cp moiety, has a relatively high enthalpy of activation. This process probably occurs through an intermediate or transition state having η^3-coordination. There is no direct evidence for the formation of such an intermediate, but some insight is provided by the fact that at 263 K a second fluxional process is observed in the ^{1}H NMR spectrum (80 MHz). At this temperature one observes the coalescence of all the resonances of the indene, giving to the AA'BB'XX'Y spectral pattern shown in Fig. 2.

Higher-temperature measurements were inhibited by the fast transformation of the η^1-complex into the carbonylated product. The spectrum of Fig. 3 can be explained if the metal undergoes a rapid 1,3-exchange through an η^3-species in which COD is monodentate and the Ir maintains its 18-electron shell. At higher temperatures complete dissociation of COD occurs, to allow rearomatization of the cyclopentadienyl ring and formation of the substitution product.

Acknowledgments

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