from the X-ray photographic method using Weissenberg and precession cameras, where a quick adjustment method for the crystal orientation was used.[10] A crystal of 2 was mounted on a computer-controlled Enraf-Nonius CAD-4 X-ray diffractometer with graphite-monochromated Mo Kα radiation. The cell dimensions and the orientation matrix were determined by least-squares calculations based on the setting angles of 25 reflections with $6.67 < \theta < 14.30°$. The crystallographic parameters are summarized in Table III. The intensities were collected at room temperature up to $\theta = 25°$ corresponding to $(\sin \theta)/\lambda = 0.59$ Å^{-1} with ω–2θ scan mode and ω scan width $(0.8 + 0.14 \tan \theta)°$. One standard reflection ($\bar{2}34$) was monitored after every $1^1/_2$ h of exposure and showed no apparent variation during data collection. The orientation matrix was checked every 100 reflections.

The intensities were corrected for Lorentz–polarization but not for absorption or extinction. Atomic scattering factors f' and f'' were taken from ref 11.

The structure was solved by using Patterson and direct methods,[12] which revealed the position of the Mo atom. The remaining heavy atoms and also all hydrogen atoms were located in successive difference Fourier syntheses. All heavy atoms were refined anisotropically, but H atoms were refined isotropically. The structure was refined by using full-matrix least-squares methods with the SHELX program.[13] All calculations were carried out on a MV/10000 computer at the computer center of Chungnam National University. Table IV lists the final atomic parameters and their estimated standard deviations. The drawing of the molecular geometry was made with the ORTEP program.[14]

Acknowledgment. Financial support from the Korea Science and Engineering Foundation is gratefully acknowledged.

Registry No. 2, 104083-32-1.

Supplementary Material Available: Tables listing complete interatomic distances and angles, anisotropic thermal parameters, isotropic thermal parameters for hydrogen atoms, and least-squares planes and deviations of individual atoms from the planes and a figure showing a unit cell packing diagram as viewed down the *c* axis (8 pages); a table of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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[10] (a) Suh, I. H.; Suh, J. M.; Ko, T. S.; Aoki, K.; Yamazaki, H. *J. Appl. Crystallogr.* **1988**, *21*, 521. (b) Suh, I. H.,; Suh, J. M.; Ko, T. S.; Aoki, K.; Yamazaki, H. *J. Appl. Crystallogr.* **1989**, *22*, 521.

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Unexpected Synthesis of CpIr(η^4-C_5H_6) and a ^{1}H and ^{13}C NMR Comparison with Its Cobalt and Rhodium Congeners

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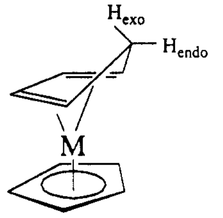
Summary: The complex CpIr(η^4-C_5H_6) was prepared unexpectedly in up to 37% yield from the reaction of $[(\eta^2\text{-}C_8H_{14})_2IrCl]_2$ and thallium cyclopentadienide. The ^{1}H NMR resonance for the exo methylene proton of the coordinated cyclopentadiene ring is shifted well downfield of what is observed for the analogous Co and Rh complexes. Complete proton and carbon NMR assignments for all three complexes were determined by ^{1}H–^{13}C correlation experiments. The H_{exo}/H_{endo} assignment for CpIr(η^4-C_5H_6) was supported by a ^{1}H–^{1}H NOE experiment and by the preparation of CpIr(η^4-C_5H_5D) from $[Cp_2Ir^+]$.

As part of our recent work involving Ir(I) olefin complexes,[1] we attempted to prepare the cyclooctene complex CpIr(η^2-C_8H_{14})$_2$[2] from the reaction of $[(\eta^2\text{-}C_8H_{14})_2IrCl]_2$ with thallium cyclopentadienide in diethyl ether. However, the isolated product proved to be the cyclopentadiene complex CpIr(η^4-C_5H_6), which had been reported by Fischer in 1959.[3] Although the use of ^{1}H NMR spectroscopy to characterize the cyclopentadiene complexes CpM(η^4-C_5H_6), M = Co, Rh,[4] constituted one of the earliest applications of this technique in organometallic chemistry, the spectrum of CpIr(η^4-C_5H_6) has not been previously reported. Coordination of the cyclopentadiene ring to a metal center places the methylene protons into separate "exo" and "endo" positions (see I), and interest in these compounds relates to the differential physical and chemical properties of the C–H_{exo} and C–H_{endo} bonds. For the purposes of comparison we present ^{1}H and ^{13}C NMR data for the entire set of congeneric complexes CpM(η^4-C_5H_6), M = Co, Rh, Ir, obtained with modern one- and two-dimensional NMR techniques.



I

Experimental Section

General Data. All synthetic manipulations were conducted under an atmosphere of nitrogen by using standard Schlenk techniques. CpCo(η^4-C_5H_6) and CpRh(η^4-C_5H_6) were prepared by the method of Green et al.[4] $[(\eta^2\text{-}C_8H_{14})_2IrCl]_2$[5] and thallium

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[1] Szajek, L. P.; Lawson, R. J.; Shapley, J. R. *Organometallics* **1991**, *10*, 357.

[2] CpIr(η^2-C_8H_{14})$_2$ has been prepared by using CpLi: Dziallis, M.; Hohn, A.; Werner, H. *J. Organomet. Chem.* **1987**, *330*, 207.

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[4] Green, M. H. L.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1959**, 3758.

[5] Nielson, A. J.; Richard, C. E. F.; Smith, T. M. *Inorg. Synth.* **1978**, *24*, 97.

Table I. ^{1}H NMR Data for CpM(η^4-C_5H_6) Complexes

	chemical shifts, δ (coupling consts, Hz)				
metal	H_{endo}	H_{exo}	H_2	H_3	H_{Cp}
Co	2.61, d (J_{gem} = 13.9)	1.83, d (J_{gem} = 13.9)	2.48, s	5.37, s	4.71, s
Rh	2.77, m (J_{gem} = 12.1) (J_{vic} = 2.1) (J_{RhH} = 1.0)	3.21, d (J_{gem} = 12.1)	3.27, m (J_{HH} = 2.1) (J_{RhH} = 1.3)	5.20, m (J_{HH} = 1.4) (J_{RhH} = 1.8)	5.17, d (J_{RhH} = 0.8)
Ir	3.17, dt (J_{gem} = 9.5) (J_{vic} = 2.1)	5.57, d (J_{gem} = 9.5)	3.13, m (J_{HH} = 1.5)	4.88, m (J_{HH} = 1.5)	5.13, s

cyclopentadienide[6] were prepared by literature methods. "Super Deuteride", a 1 M solution of $LiBEt_3D$ in THF, was used as received from the Aldrich Chemical Co. Solvents for preparative use were dried by using standard methods and distilled immediately before use. Deuterated chloroform was distilled from phosphorus pentoxide and then passed through a short column of activated basic alumina immediately before being used to prepare NMR samples.

^{1}H, ^{13}C (125 MHz), and correlation NMR spectra were recorded on a General Electric GN-500 NMR FT spectrometer in $CDCl_3$. IR spectra were recorded on a Perkin Elmer Model 1750 FT spectrometer. The 70-eV electron-impact mass spectrum was recorded on a Finnegan MAT CH7 spectrometer by the staff of the Mass Spectrometry Laboratory. Microanalyses were preformed by the staff of the Microanalytical Laboratory.

CpIr(η^4-C_5H_6). To a yellow suspension of $[(\eta^2\text{-}C_8H_{14})_2IrCl]_2$ (250 mg, 0.28 mmol, 0.56 mmol of Ir) in diethyl ether (100 mL) at 0 °C was added thallium cyclopentadienide (160 mg, 0.59 mmol). An orange solution was formed immediately, which was stirred for an additional 4 h. Decolorizing carbon was added, and the mixture was filtered via a filter cannula. The red filtrate was reduced in volume to ca. 5 mL, placed on a column (20 × 2 cm) of activated neutral alumina, and eluted with diethyl ether (100 mL). The eluate was reduced to dryness, and the pale red residue was sublimed at 100 °C (10^{-1} Torr) to a water-cooled cold-finger. The white crystalline sublimate was collected. Yield: 35 mg, 0.11 mmol (37% based on CpTl). Mp (sealed tube): 125–127 °C (lit.[3] 130–132 °C). IR (KBr, 3200–2000 cm^{-1}): 3085 (m), 3044 (m), 2956 (m), 2891 (m), 2776 (s), 2754 (s) cm^{-1}. Anal. Calcd for $IrC_{10}H_{11}$: C, 37.14; H, 3.43. Found: C, 37.18; H, 3.35. EI-MS (70 eV, 25 °C): *m/z* (^{193}Ir) 323 M$^+$.

When the analogous reaction was conducted with $[(\eta^2\text{-}C_8H_{14})_2IrCl]_2$ (250 mg, 0.28 mmol, 0.56 mmol of Ir) in diethyl ether (100 mL) and 2 equiv of thallium cyclopentadienide per iridium (320 mg, 1.1 mmol, 0.59 mmol of Ir), analytically pure CpIr(η^4-C_5H_6) was obtained in reduced yield (24% based on CpTl).

CpIr(η^4-C_5H_5D). To a stirred solution of CpIr(η^4-C_5H_6) (50.0 mg, 0.15 mmol) in THF (5 mL) was added triphenylcarbenium hexafluorophosphate (60.0 mg, 0.15 mmol). The orange color of the solution was immediately discharged, and a white powder precipitated. After 0.5 h the reaction mixture was reduced to dryness, and the yellow residue was extracted with cyclohexane (10 mL) to remove triphenylmethane and unreacted CpIr(η^4-C_5H_6). A ^{1}H NMR spectrum of the residual white powder showed a singlet at δ 5.98, consistent with the reported resonance of $[Cp_2Ir]PF_6$.[7] THF (5 mL) was added to dissolve the remaining solid, and $LiBEt_3D$ (150 μL, 0.15 mmol) was added to the rapidly stirred solution. The solution effervesced and slowly turned orange-red. After 0.5 h the solvent was evaporated, and the pale red residue was worked up by chromatography and sublimation as described above (23 mg, 0.11 mmol, 44%). IR (KBr, 3200–2000 cm^{-1}): 3079 (s), 3057 (s), 2956 (s), 2920 (m), 2852 (m), 2065 (m), 2038 (m) cm^{-1}.

Results

The preparation of CpIr(η^4-C_5H_6) reported here is not particularly efficient in either reactant, although it does represent a practical advance over the original report of 1% yield starting with anhydrous $IrCl_3$.[3] Our highest yield of 37% for CpIr(η^4-C_5H_6) was obtained with a 1:1 ratio of CpTl:Ir in diethyl ether; curiously, the yield decreased to 24% with a 2:1 ratio of CpTl:Ir. Lower yields of CpIr(η^4-C_5H_6) were obtained with THF as solvent.

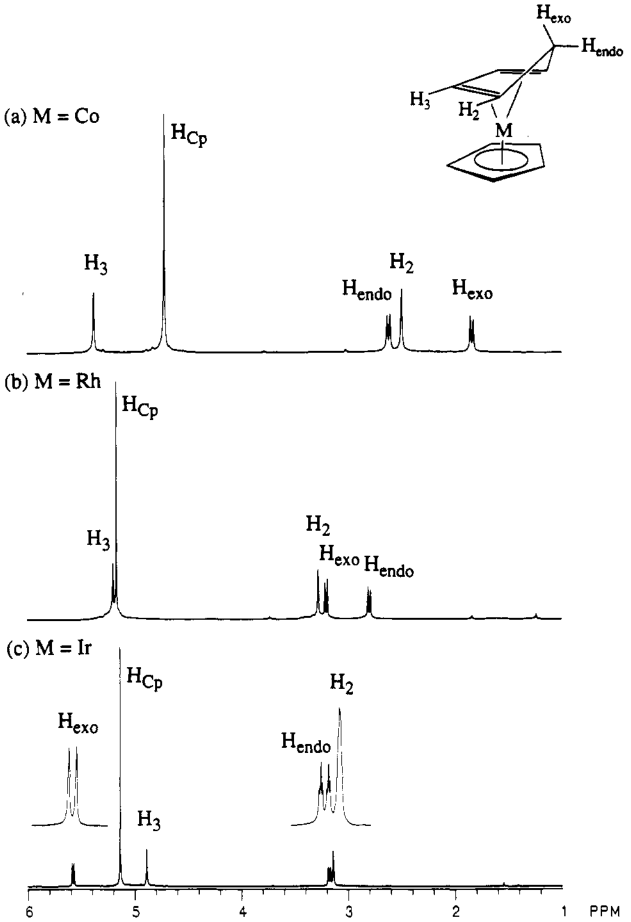

Figure 1. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of CpM(η^4-C_5H_6) complexes: (a) Co; (b) Rh; (c) Ir.

The deuterated complex CpIr(η^4-C_5H_5D) was prepared by hydride abstraction from CpIr(η^4-C_5H_6) with $[Ph_3C]PF_6$ in THF to form $[Cp_2Ir^+]$[7] followed by deuteride addition with $LiBEt_3D$. The solid-state infrared spectrum of CpIr(η^4-C_5H_5D) shows C–D stretches at 2065 and 2038 cm^{-1}, replacing the intense pair of bands at 2776 and 2754 cm^{-1} seen in the spectrum of CpIr(η^4-C_5H_6). Since the latter feature can be attributed to C–H_{exo}, the deuterium position in CpIr(η^4-C_5H_5D) is exo, as expected (vide infra).[8-11] A higher energy band at 2956 cm^{-1} present in both spectra can be attributed to the C–H_{endo} stretching mode. Spectral traces of both species in the region 2000–3200 cm^{-1} are included as supplementary material.

The ^{1}H NMR spectrum for CpIr(η^4-C_5H_6) is shown in Figure 1 along with the high-field spectra of the analogous Co and Rh complexes for comparison. The spectrum of CpIr(η^4-C_5H_6) shows the 5:2:2:1:1 intensity pattern expected for the formulation, but proper integration is dif-

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[7] Fischer, E. O.; Wawersik, H. *J. Organomet. Chem.* **1966**, *2*, 207.

[8] Moseley, K.; Kang, J. W.; Maitlis, P. M. *J. Chem. Soc. A* **1970**, 2875.

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[11] Schrock, R. R.; Osborn, J. A. *Inorg. Chem.* **1970**, *9*, 2339.

Table II. ^{13}C NMR Data for $CpM(\eta^4\text{-}C_5H_6)$ Complexes

	chemical shifts, δ (coupling consts, Hz)			
metal	C_1	C_2	C_3	C_{Cp}
Co	40.6 ($J_{CH} \approx 125$)	38.5 (J_{CH} = 170)	76.3 (J_{CH} = 175)	78.7 (J_{CH} = 175)
Rh	44.7 (J_{CRh} = 4.8)	41.5 (J_{CRh} = 11.9)	75.4 (J_{CRh} = 9.4)	82.6 (J_{CRh} = 5.3)
Ir	46.1 (J_{CH} = 125) ($J_{CH'}$ = 123)	23.9 (J_{CH} = 170)	63.8 (J_{CH} = 180)	75.5 (J_{CH} = 179)

ficult unless a relatively long pulse delay is used. This is due to the large difference in relaxation time for the methylene protons relative to the methyne protons. For H_{exo} and H_{endo}, T_1 is 5–6 s, while for H_{Cp}, H_2, and H_3, T_1 is in the range 16–21 s, with the value decreasing in the order Co > Rh > Ir. Table I summarizes the chemical shift and coupling constant data for the set of complexes.

Assignment of the separate methylene proton resonances in the spectrum of $CpIr(\eta^4\text{-}C_5H_6)$ to H_{exo} and H_{endo} rests on three related considerations. (1) The signal at δ 5.57 is observed as a doublet due to geminal coupling, whereas the signal at δ 3.17 is a doublet of triplets due to an additional, observable coupling to the olefin protons (H_2). This minor coupling is also observed for the multiplet at δ 2.77 in the spectrum of $CpRh(\eta^4\text{-}C_5H_6)$. (2) In the ^1H NMR spectrum of the deuterated complex $CpIr(\eta^4\text{-}C_5H_5D)$ the resonance at δ 5.57 is not observed and the signal at δ 3.17 now appears as a singlet. (3) Irradiation of the cyclopentadienyl proton signal indicated a slight Overhauser enhancement of the signal at δ 3.17 compared to the resonance at δ 5.57.

Two-dimensional correlation spectroscopy was used to assign the ^{13}C NMR resonances; the results are summarized in Table II. For $CpIr(\eta^4\text{-}C_5H_6)$ an attached proton test (APT) spectrum distinguishes the methylene resonances C_1 (positive) from the methylene resonances of C_2, C_3, and C_{Cp} (negative), as shown in Figure 2. These resonances then can be correlated to their attached proton resonances by tracing the cross peaks in the ^1H–^{13}C heteronuclear correlation (HETCOR) spectrum, again shown for $CpIr(\eta^4\text{-}C_4H_6)$ in Figure 2. The HETCOR spectrum shows unambiguously that the two ^1H signals at δ 5.57 and 3.17 correspond to the methylene protons of the coordinated cyclopentadiene ring. This correlation is also observed in the ^1H–^1H correlation (COSY) spectrum of $CpIr(\eta^4\text{-}C_5H_6)$ with an intense cross peak for the two methylene resonances along with a weaker correlation between H_2 and H_3. A similar analysis was completed for the analogous Rh and Co complexes and the 2D spectra are included as supplementary material.

The differential bonding of H_{exo} and H_{endo} is observed as a differential $^1J_{CH}$ coupling in the ^{13}C NMR spectrum of $CpIr(\eta^4\text{-}C_5H_6)$ when no broad-band decoupling is applied (see supplementary material). The C_1 resonance is observed as a doublet of doublets, with one coupling of 125.0 Hz and the other a slightly smaller coupling of 123.6 Hz. This differential $^1J_{CH}$ coupling is not well resolved for $CpCo(\eta^4\text{-}C_5H_6)$, due to broader lines.

Discussion

In the first studies of the cyclopentadiene complexes $CpM(\eta^4\text{-}C_5H_6)$ where M = Co,[4] Rh,[3,4] and Ir[3] the structures were deduced on the basis of infrared and ^1H NMR spectroscopy. An unusual, the low-energy IR band at ca. 2750 cm^{-1} was attributed to an interaction of H_{endo} with the metal center.[4] Since the band was absent in substituted complexes, generated by nucleophilic attack on $[Cp_2Co^+]$, the substituent was assumed to be in the endo position. However, subsequent X-ray crystallographic studies on $CpCo(\eta^4\text{-}C_5H_5C_6H_5)$[9] and $CpCo(\eta^4\text{-}C_5H_5\text{-}(CO)C_6H_5)$[10] revealed that the substituents occupy the exo position relative to the metal center, thereby requiring reassignment of the unusual IR band to C–H_{exo}. Other structural studies[12] have substantiated this conclusion, most recently that of Jones and Maguire[13] on $H_3Re(PPh_3)_2(\eta^4\text{-}C_5H_6)$, the structure of which showed conclusively that the Re···H_{endo} distance of 3.18 Å is indeed too long to infer that a M···H interaction is responsible for the low-energy ν_{CH} stretch.

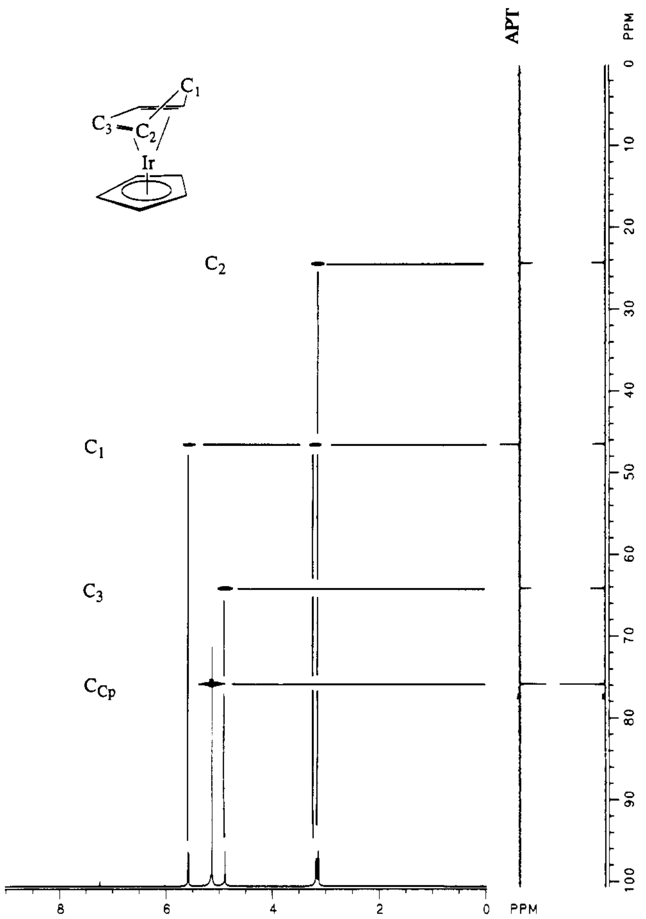

Figure 2. APT and HETCOR spectra of $CpIr(\eta^4\text{-}C_5H_6)$.

Specific assignment of the ^1H NMR signals to the exo and endo methylene protons can be based on the magnitude of vicinal coupling to the neighboring olefin protons,[11,14] since structural studies[9,10,13] suggest a small dihedral angle (ca. 0°) for H_2···H_{endo} and a large angle (ca. 90°) for H_2···H_{exo}. Similar considerations were apparently applied in suggesting assignments for the ^1H NMR signals of $(C_5Me_5)Ir(\eta^4\text{-}C_5H_6)$,[8] but few details were given. We have used a combination of experiments in order to completely assign the proton resonances of $CpIr(\eta^4\text{-}C_5H_6)$ and thereby complete a study of a congeneric set of complexes, $CpM(\eta^4\text{-}C_5H_6)$ where M = Co, Rh, Ir. Figure 3 illustrates the trends in proton chemical shifts for the three complexes as a function of metal.

The first point to note from Figure 3 is that the resonance position of H_{exo} vs H_{endo} is upfield for the cobalt complex but downfield for the rhodium complex. Given the endo/exo confusion in the original paper,[4] this reversal

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[12] (a) Bird, P. H.; Churchill, M. R. *J. Chem. Soc., Chem. Commun.* 1967, 777. (b) Alcock, N. W. *J. Chem. Soc., Chem. Commun.* 1965, 177.

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[14] (a) Davies, S. G.; Moon, S. D.; Simpson, S. J.; Thomas, S. E. *J. Chem. Soc., Dalton Trans.* 1983, 1805. (b) Davies, S. G.; Simpson, S. J.; Felkin, H.; Fillebeen-Khan, T. *Organometallics* 1983, 2, 539.

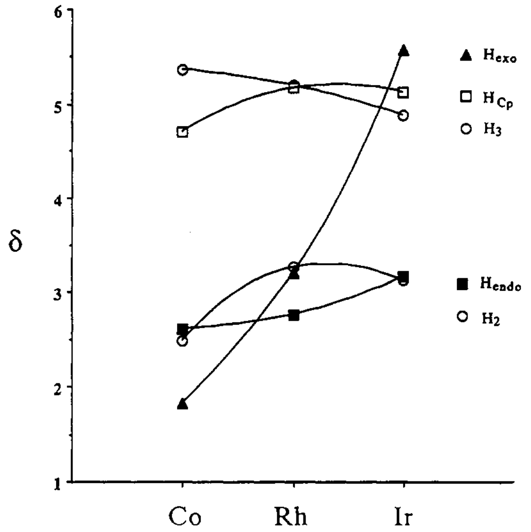


Figure 3. Proton chemical shifts vs metal for CpM(η^4-C_5H_6) complexes.

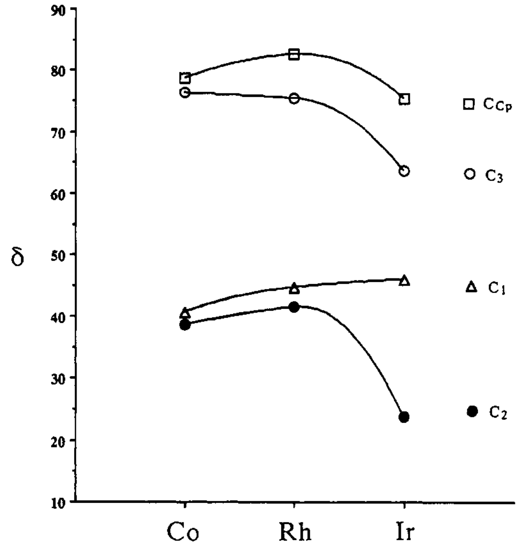
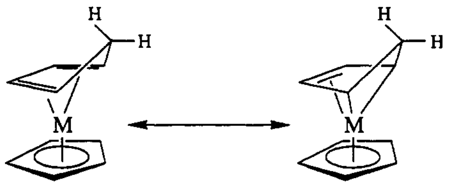


Figure 4. Carbon chemical shifts vs metal for CpM(η^4-C_5H_6) complexes.

has not been appreciated in subsequent tabulations;[14b] however, a similar reversal is also apparent in comparing analogous iron and ruthenium cyclopentadiene complexes.[14] Certainly, the most striking trend in the data shown in Figure 3 is the dramatic downfield shift of the H_{exo} signal for the iridium complex. No comparable study of a complete triad is available,[15] but the strongly downfield position for H_{exo} may be general for third-row transition-metal complexes, since the H_{exo}/H_{endo} chemical shifts suggested for both (C_5Me_5)Ir(η^4-C_5H_6) (δ 5.63/δ 3.68)[8] and H_3Re(PPh_3)$_2$(η^4-C_5H_6) (δ 5.76/δ 3.53)[13] are very similar to those observed in this study.

Figure 4 illustrates the trends in carbon chemical shifts for the three complexes. Again, the iridium complex shows an anomaly in the significant upfield chemical shift of C_2. The positions of the ^{13}C NMR signals for the iridium complex may be explained in terms of the well-known hybrid bonding model for olefin coordination to a transition-metal complex.[16] In the particular case of a conjugated diene, the metal–diene bonding interaction is described as a resonance hybrid between a structure with π-bonds (II) and a structure with two σ-bonds and a donor



II III

π-bond (III). In molecular orbital orbital terms the former structure represents the donor portion and the latter the π-acceptor portion of the bonding interaction.[10] The iridium complex apparently favors the latter resonance form to a greater degree than either the cobalt or rhodium complexes. This is consistent with other evidence that Ir(I) shows a greater degree of π-back-bonding than analogous Rh(I) complexes.[1] To what extent the bonding change is accompanied by a distinct structural change, e.g., in the fold angle of the cyclopentadiene ring, is not clear in the absence of structural data. It is worth noting, however, that the fold angle of 143.8° determined for the complex H_3Re(PPh_3)$_2$(η^4-C_5H_6)[13] is essentially identical with that established previously for CpCo(η^4-$C_5H_5C_6H_5$).[9]

Acknowledgment. This research was supported by the National Science Foundation Grant CHE 89-15349.

Supplementary Material Available: IR (KBr) spectra of CpIr(η^4-C_5H_6) and CpIr(η^4-C_5H_5D), ^1H-^1H COSY spectra of CpM(η^4-C_5H_6) (M = Co, Rh, Ir), ^1H-^{13}C HETCOR spectra of CpM(η^4-C_5H_6) (M = Co, Rh), and $^{13}C\{^1H$-coupled$\}$ NMR spectrum of CpIr(η^4-C_5H_6) (7 pages). Ordering information is given on any current masthead page.

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(15) A small sample of $Os(CO)_3$(η^4-C_5H_6) has been prepared, but NMR characterization was incomplete: Humphries, A. P.; Knox, S. A. R. *J. Chem. Soc., Dalton Trans.* **1975**, 1710.

(16) Green, M. H. L.; Coates, G. E.; Wade, K. *Organometallic Compounds*; Methuen & Co. Ltd.: London, 1968; Vol. 2, p 302.