Solid-state structure and fluxional solution behavior of the ambident organometallic nucleophiles (.eta.3-C7H7)M(CO)3- (M = ruthenium, osmium)

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tolysis. Within experimental error, the relative amounts of the three isomers remained constant.

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Registry No. **6c**, 114944-66-0; **6d**, 114944-67-1; **6e**, 123724-41-4; **6f**, 123724-44-7; *trans*-**6g**, 123724-50-5; *cis*-**6g**, 123807-09-0; *trans*-**6h**, 123724-45-8; *cis*-**6h**, 123807-06-7; **8c**, 114944-68-2; **9c**, 114944-69-3; **9d**, 114944-70-6; *exo*-**10c**, 114944-72-8; **10e**, 123724-43-6; *exo,syn*-**10g**, 35429-53-9; *exo,anti*-**10g**, 35429-52-8; *exo,anti*-**10h**, 123724-46-9; *endo,syn*-**10h**, 123807-07-8; *endo,anti*-**10h**, 123807-08-9; *exo,syn*-**10h**, 123807-11-4; *exo,syn*-**11c**, 114944-71-7; **12**, 123724-42-5; *trans*-**13**, 123724-51-6; *cis*-**13**, 123807-10-3; KFp, 60039-75-0; [CpFe(CO)$_2$(η^2-CH$_2$=CHCH$_2$F)]BF$_4$, 123724-49-2; dicarbonyl(η^5-cyclopentadienyl)(η^1-*cis*-1-fluoropropenyl)iron, 123724-47-0; 1-bromo-1-ethoxycyclopropane, 95631-62-2; 1-iodo-1-(phenylthio)cyclopropane, 123724-40-3; *trans*-1-bromo-2-fluorocyclopropane, 116577-38-9; *trans*-2-methylcyclopropyl bromide, 6142-48-9; epifluorohydrin, 503-09-3; *cis*-2-methylcyclopropyl bromide, 6142-60-5; 2-methylcyclopropanecarboxylic acid chloride, 60733-34-8; 2-methylcyclopropanecarboxylic acid, 29555-02-0; oxalyl chloride, 79-37-8.

Solid-State Structure and Fluxional Solution Behavior of the Ambident Organometallic Nucleophiles (η^3-C_7H_7)M(CO)$_3^-$ (M = Ru, Os)

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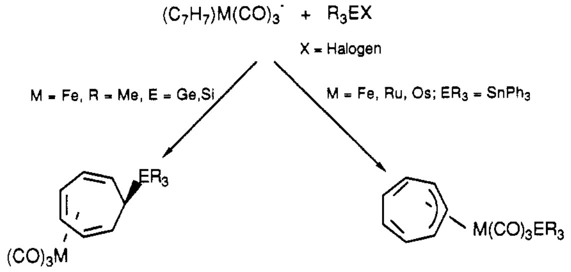
The cycloheptatrienyl carbonyl anions (C_7H_7)M(CO)$_3^-$ (M = Ru, **1b**; M = Os, **1c**) have been isolated and structurally characterized as their Ph_4As^+ salts. Both **1b** and **1c** crystallize in the centrosymmetric space group $P\bar{1}$ with two molecules per unit cell. For **1b**: a = 12.308 (4) Å, b = 12.017 (5) Å, c = 11.326 (4) Å, α = 71.18 (2)°, β = 80.93 (2)°, γ = 90.15 (2)°. For **1c**: a = 12.314 (2) Å, b = 12.025 (2) Å, c = 11.331 (2) Å, α = 71.12 (2)°, β = 80.87 (2)°, γ = 90.08°. The structures were refined to $R(F)$ = 0.0567 and 0.0268 and $R_w(F)$ = 0.0575 and 0.0278 for 3686 and 3905 reflections with $F > 3.0\sigma(F)$ for **1b** and **1c**, respectively. In both cases the seven-membered ring is coordinated to the metal in an η^3 fashion. The low-temperature-limiting ^{1}H and ^{13}C NMR spectra of **1c** have been obtained and show that the same bonding mode is also adopted in solution. A comparison of the spectroscopic, structural, and chemical properties for the series of complexes (C_7H_7)M(CO)$_3^-$ (M = Fe, Ru, Os) is made and explained in terms of increasing metal basicity upon descending the triad.

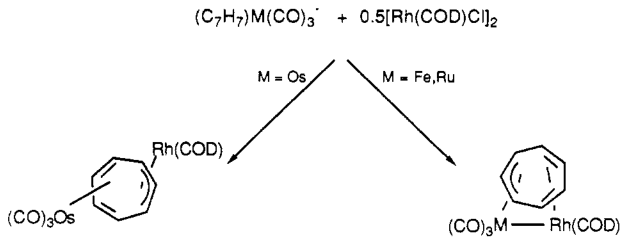
Introduction

Anionic complexes of the transition metals are generally highly reactive species and offer a simple route to the preparation of new metal–carbon[1] and metal–metal[2] bonds. We have for some time been involved in a systematic investigation of the chemistry of the anionic complexes (C_7H_7)M(CO)$_3^-$ (**1**) [M = Fe (**1a**), Ru (**1b**), Os (**1c**)]. The ambident nature of **1** manifests itself in an interesting and metal-dependent fashion. Thus the reaction with R_3SiCl and R_3GeBr gives ring-substituted complexes,[3] whereas Ph_3SnCl results in fluxional η^3-C_7H_7 complexes containing a M–Sn bond[4] (Scheme I). In accord with the reaction of Ph_3SnCl, transition-metal-based electrophiles were found to react with **1a** and **1b** to give cycloheptatrienyl-bridged heterobimetallic complexes[4b,5] where the two metals occupy the same face of the ring. However, recent discoveries indicated that the reaction of **1c** with [Rh(C-

Scheme I



Scheme II



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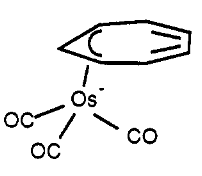
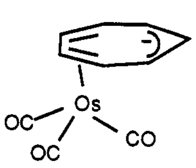
OD)Cl]$_2$ gives the isomeric unsaturated complex where Os and Rh are bonded to opposite faces of the C_7H_7 ligand[6] (Scheme II).

A possible reason for the variable reactivity exhibited by complexes **1** could be the availability, on the basis of the effective atomic number rule, of two bonding alternatives between the ring and the metal carbonyl fragment. These are as follows:



A



B

Changes in the predominant structural form in solution with the transition metal or differential sampling of the two forms by the electrophilic reagents could be the reason for the observed reactivity. Alternatively, it is also possible that changes in the interactions between the organic and inorganic partners, in either form, as the metal is varied and the attendant changes in charge distribution, could be the sole reason for the electrophilic discrimination displayed by complexes **1**.

Clearly, in order to rationalize the observed reactivities, a precise knowledge of the bonding between the seven-membered ring and the metal tricarbonyl fragment is necessary, both in the solid state and in solution. The solid-state structure of **1a** has been determined and shown to conform to form A.[7] The ground-state structural preference for the η^3-bonded cycloheptatrienyl ring was also demonstrated by extended Hückel MO calculations.[8] Surprisingly, for **1a** it was found that there is more charge localization on the ring in structure A than in the η^4-bonding alternative (B) which features a "free" allyl anion fragment. However, the calculations also showed that the η^4-bonded structure (B) is only slightly less stable (14.2 kJ mol^{-1}) than bonding form A. The small energy difference between the two structures was used to rationalize the fluxional nature of **1a** in solution at room temperature and below. Here we wish to report the solid-state structures of compounds **1b** and **1c** and the results of variable-temperature NMR studies with a view to establish the solution structure of these anionic species.

Experimental Section

All reactions were carried out under purified nitrogen using standard Schlenk techniques and carefully dried solvents. Crystallizations of **1b** and **1c** were performed in a Vacuum Atmospheres Model M040-2 glove box under purified nitrogen. Infrared spectra were obtained with a Nicolet MX-1 Fourier Transform Interferometer. The variable temperature NMR spectra were recorded on a Bruker AM 400 spectrometer. In both instances the samples were prepared under inert atmosphere. Elemental Analysis were performed by the Microanalytical Laboratory of this department.

Synthesis of $[AsPh_4][(C_7H_7)Os(CO)_3]$ (1c). $K[(C_7H_7)Os(CO)_3]$ in THF (15 mL) was made directly from $(C_7H_8)Os(CO)_3$ (85 mg, 0.23 mmol) and KO^{t}Bu (26 mg, 0.23 mmol).[6,9] The dark red solution was transferred under nitrogen to a separate flask containing a slurry of $AsPh_4Cl$ (97 mg, 0.23 mmol) in THF (15 mL). The mixture was stirred at room temperature for 15 min and then filtered. The solvent was removed from the filtrate to leave a dark orange residue which was redissolved in THF and crystallized rapidly at room temperature by addition of toluene. This gave dark red crystals of $[AsPh_4][(C_7H_7)Os(CO)_3]\cdot THF$ (70 mg, 41%). The inclusion of one molecule of THF was determined from integration of the ^1H NMR spectrum in CD_2Cl_2.

Anal. Calcd for $C_{38}H_{35}AsO_4Os$: C, 55.55; H, 4.29. Found: C, 55.80; H, 4.38. IR (THF): ν_{CO} 1963 (s), 1883 (s), 1864 (s) cm^{-1}. ^1H NMR (25 °C, THF-d_8): δ 7.7–7.9 (20 H, Ph), 4.66 (s, 7 H, C_7H_7). ^1H NMR (−115 °C, THF-d_8): δ 6.42 (m, 2 H, H_3), 4.87 (dd, $J_{H_3-H_4}$ = 8.3, 3.7 Hz, 2 H, H_4), 3.83 (dd, $J_{H_2-H_3}$ = 7.5 Hz, $J_{H_1-H_2}$ = 4.5 Hz, 2 H, H_2), 2.19 (t, $J_{H_1-H_2}$ = 4.5 Hz, 1 H, H_1). $^{13}C\{^1H\}$ NMR (25 °C, THF-d_8): δ 191.9 (s, CO), 135.3 (s, Ph, p), 134.4 (s, Ph), 131.8 (s, Ph), 89.2 (s, C_7H_7). $^{13}C\{^1H\}$ NMR (−110 °C, THF-d_8): 142.0 (s, C_7H_7, C_3), 111.9 (s, C_7H_7, C_4), 37.9 (s, C_7H_7, $C_1 + C_2$).

Synthesis of $[AsPh_4][(C_7H_7)Ru(CO)_3]$ (1b). $K[(C_7H_7)Ru(CO)_3]$ was prepared according to the literature procedure.[4b] The exchange of K^+ for Ph_4As^+ was carried out in similar fashion to the preparation of **1c**. The resultant red residue was then crystallized from THF/hexane at −40 °C to give large, dark red crystals of $[AsPh_4][(C_7H_7)Ru(CO)_3]\cdot THF$ (**1b**) (0.72 g, 61%).

Anal. Calcd for $C_{38}H_{35}AsO_4Ru$: C, 62.38; H, 4.82. Found: C, 62.69; H, 4.32. IR (THF): ν_{CO} 1960 (s), 1885 (s), 1864 (s) cm^{-1}. ^1H NMR (25 °C, THF-d_8): δ 7.7–7.9 (20 H, Ph), 4.58 (s, 7 H, C_7H_7). ^{13}C NMR (25 °C, CD_2Cl_2): δ 213.0 (s, CO), 135.1 (s, Ph, p), 133.1 (s, Ph), 131.6 (s, Ph), 92.7 (s, C_7H_7).

Crystallographic Studies. General operating procedures and listings of programs have been previously given.[10]

$[AsPh_4][(C_7H_7)Ru(CO)_3]\cdot 0.5C_7H_8$ (1b). X-ray quality crystals were obtained from THF/toluene over 1 week at −40 °C. A suitable crystal was located and transferred to the goniostat by using standard inert atmosphere handling techniques and cooled to −155 °C for characterization and data collection. A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with no symmetry or systematic absences, indicating one of the triclinic space groups. Subsequent solution and refinement of the structure confirmed the centrosymmetric choice $P\bar{1}$.

Data were collected in the usual manner by using a continuous θ–2θ scan with fixed backgrounds. Data were reduced to a unique set of intensities and associated σ's in the usual manner. The structure was solved by a combination of direct methods (MULTAN78) and Fourier techniques.

The compound of interest cocrystallizes with 0.5 molecule of toluene per asymmetric unit, the toluene molecule being on a crystallographic center of symmetry. The methyl group on the toluene molecule is therefore disordered. A difference map revealed all of the hydrogen atoms except for the disordered methyl group. All hydrogen atoms which had been located were refined isotropically and non-hydrogen atoms anisotropically in the final cycles. No absorption correction was performed. A final difference Fourier was featureless, with the largest peak being 0.45 e/Å^3.

$[AsPh_4][(C_7H_7)Os(CO)_3]\cdot 0.5C_7H_8$ (1c). Crystals were grown from THF/toluene at room temperature over 2 days. A suitable crystal was mounted by using silicone grease in a nitrogen atmosphere glovebag and was transferred to a goniostat where it was cooled to −143 °C for characterization and data collection. A systematic search of a limited hemisphere of reciprocal space revealed no symmetry or systematic absences. A triclinic unit cell was found which was very similar to that of **1b**, indicating that the present structure was probably isomorphous with the earlier one. There was no need to solve the structure. The coordinates for the non-hydrogen atoms in **1b** were used as a starting point and they quickly refined to an $R(F)$ = 0.033. In the final cycles of refinement, the hydrogen atoms that had been located (i.e. all, except those of the disordered methyl group of the toluene solvate) were refined with isotropic thermal parameters and the non-hydrogen atoms were refined with anisotropic thermal parameters. No absorption correction was applied. The final difference map was essentially featureless. There were heavy-atom

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Table I. Summary of Crystallographic Data

	1b	1c
empirical formula	$RuAsC_{34}H_{27}\cdot 0.5C_7H_8$	$OsAsC_{34}H_{27}\cdot 0.5C_7H_8$
color of cryst	red	red
cryst dimens, mm	0.25 × 0.25 × 0.25	0.1 × 0.2 × 0.3
space group	$P\bar{1}$	$P\bar{1}$
cell dimens (−155 °C)		
a, Å	12.308 (4)	12.314 (2)
b, Å	12.017 (5)	12.025 (2)
c, Å	11.326 (4)	11.331 (2)
α, deg	71.18 (2)	71.12 (1)
β, deg	80.93 (2)	80.87 (1)
γ, deg	90.15 (2)	90.08 (1)
Z (molecules/cell)	2	2
V	1563.23	1564.85
d(calcd), g/cm^3	1.499	1.700
wavelength λ, Å	0.71069	0.71069
mol wt	705.65	800.78
linear abs coeff, cm^{-1}	15.734	51.597
detector to sample dist, cm	22.5	22.5
sample to source dist, cm	23.5	23.5
av ω scan width at half-height, deg	0.25	0.25
scan speed, deg/min	8.0	6.0
scan width, deg + dispersn	1.8	1.8
individual bkgd, s	4	6
aperture size, mm	3.0 × 4.0	3.0 × 4.0
2θ range, deg	6–45	6–45
total no. of reflctns collected	4129	7420
no. of unique intensities	4081	4106
no. of $F > 0.0$	3928	4024
no. of $F > 3.0\sigma(F)$	3686	3905
R for averaging	0.030	0.018
$R(F)$	0.0567	0.0268
$R_w(F)$	0.0575	0.0278
goodness of fit for the last cycle	1.645	1.060
max Δ/σ for the last cycle	0.35	0.52

Table II. Fractional Coordinates[a] and Equivalent Isotropic Thermal Parameters for $(C_7H_7)Ru(CO)_3^-$ in 1b

atom	*x*	*y*	*z*	B_{iso},[b] Å^2
Ru	638.4 (4)	2710.7 (5)	7794 (1)	16
C1	343 (6)	1898 (7)	6466 (7)	23
C2	−369 (6)	2858 (6)	6283 (7)	20
C3	−1573 (6)	2747 (7)	6657 (7)	24
C4	−2244 (6)	1841 (7)	7469 (8)	24
C5	−1919 (6)	749 (7)	8261 (8)	28
C6	−885 (6)	396 (6)	8389 (8)	25
C7	169 (6)	957 (6)	7640 (7)	22
C8	1869 (6)	2123 (6)	8582 (7)	24
C9	1306 (6)	4249 (7)	6920 (7)	26
C10	−529 (6)	2803 (6)	9121 (7)	20
O1	2649 (4)	1826 (5)	9032 (5)	33
O2	1738 (5)	5158 (5)	6409 (7)	48
O3	−1260 (4)	2852 (5)	9854 (5)	30

[a] Fractional coordinates are ×10^4. B_{iso} values are ×10. [b] Isotropic values for those atoms refined anisotropically are calculated by using the formula given by; Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

residuals of less then 2 e/Å^3. All other residual peaks were less than 0.5 e/Å^3. A summary of the crystallographic data for compounds **1b** and **1c** is presented in Table I. Positional and equivalent isotropic parameters of the anion $(C_7H_7)M(CO)_3^-$ are given in Tables II and III. Additional information is available as supplementary material.

Results

Table III. Fractional Coordinates[a] and Equivalent Isotropic Thermal Parameters for $(C_7H_7)Os(CO)_3^-$ in 1c

atom	*x*	*y*	*z*	B_{iso},[b] Å^2
Os	653.6 (2)	2716.0 (2)	7788.8 (2)	13
C1	346 (4)	1878 (5)	6478 (5)	20
C2	−384 (4)	2840 (5)	6297 (5)	19
C3	−1580 (5)	2736 (5)	6665 (6)	21
C4	−2247 (5)	1828 (5)	7473 (5)	23
C5	−1924 (5)	730 (5)	8275 (6)	25
C6	−897 (5)	389 (5)	8388 (6)	24
C7	1310 (5)	4254 (5)	6925 (6)	25
C8	1886 (4)	2146 (5)	8578 (5)	21
C9	1310 (5)	4254 (5)	6925 (6)	25
C10	−502 (4)	2809 (5)	9104 (5)	19
O1	2655 (3)	1843 (4)	9036 (4)	30
O2	1726 (4)	5180 (4)	6390 (5)	43
O3	−1224 (3)	2868 (4)	9851 (4)	27

[a] Fractional coordinates are ×10^4. B_{iso} values are ×10. [b] Isotropic values for those atoms refined anisotropically are calculated by using the formula given by; Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

Table IV. Selected Bond Lengths and Angles for Anions 1, $(\eta^3\text{-}C_7H_7)M(CO)_3$ (M = Fe, Ru, Os)

	Fe[a] (**1a**)	Ru (**1b**)	Os (**1c**)
	Bond Length		
metal radius[b]	1.16	1.25	1.26
M–C1	1.983 (10)	2.113 (7)	2.124 (5)
M–C2	2.113 (12)	2.230 (7)	2.244 (5)
M–C7	2.137 (11)	2.252 (7)	2.244 (5)
M–C8	1.780 (13)	1.901 (7)	1.900 (6)
M–C9	1.755 (13)	1.904 (7)	1.898 (6)
M–C10	1.765 (12)	1.941 (7)	1.922 (5)
C1–C2	1.432 (21)	1.432 (10)	1.448 (8)
C2–C3	1.429 (22)	1.468 (10)	1.459 (8)
C3–C4	1.305 (25)	1.350 (11)	1.348 (8)
C4–C5	1.428 (24)	1.429 (12)	1.438 (9)
C5–C6	1.344 (23)	1.358 (11)	1.342 (9)
C6–C7	1.421 (24)	1.462 (10)	1.455 (8)
C7–C1	1.412 (22)	1.425 (11)	1.439 (8)
C8–O1	1.130 (15)	1.161 (8)	1.154 (6)
C9–O2	1.163 (15)	1.142 (9)	1.155 (7)
C10–O3	1.138 (14)	1.139 (8)	1.146 (6)
	Bond Angles		
C2–M–C1	41.3	38.4 (3)	38.6 (2)
C3–M–C2	69.8	66.8 (3)	66.7 (2)
C7–M–C1	39.7	37.9 (3)	38.3 (2)
C8–M–C9	97.6	94.9 (3)	94.6 (2)
C9–M–C10	104.8	108.6 (3)	108.0 (2)
C10–M–C8	106.6	106.8 (3)	106.7 (2)
C1–C2–C3	127.9	125.4 (7)	126.2 (5)
C2–C3–C4	131.7	130.8 (7)	130.3 (6)
C3–C4–C5	125.9	126.9 (7)	127.3 (6)
C4–C5–C6	127.9	128.4 (7)	127.6 (6)
C5–C6–C7	130.3	129.0 (7)	130.5 (6)
C6–C7–C1	128.8	127.4 (7)	126.3 (5)
C7–C1–C2	117.1	119.4 (6)	117.5 (5)
M–C8–O1	175.8	176.2 (6)	177.3 (5)
M–C9–O2	177.4	177.8 (6)	178.7 (5)
M–C10–O3	179.1	175.8 (6)	176.9 (5)

[a] From ref 7. [b] From ref 11.

Solid-State Structure of $(C_7H_7)M(CO)_3^-$ Compounds. In the solid state, complexes **1b** and **1c** were found to be isomorphous and nearly isostructural. The unit cell contains well-separated Ph_4As^+ cations and $(C_7H_7)M(CO)_3^-$ anions. Two perspective views of the anionic organometallic constituent are shown in Figure 1 which also establishes the numbering system. Important bond distances and angles, together with those of **1a** for comparison, are listed in Table IV. It is clear from the figure that the cycloheptatrienyl ring is bonded to the metal in an η^3-fashion in both complexes. This type of structure has already been seen for the analogous iron compound **1a** and its stability over the alternative η^4-bonded cycloheptatrienyl form (see A and B) has also been predicted on the basis of extended Hückel MO calcula-

Table V. ^1H and ^{13}C NMR Data of the $\eta^3\text{-}C_7H_7$ Ligand in 1 and Related Complexes[a]

compd	H_1/C_1	H_2/C_2	H_3/C_3	H_4/C_4	temp, °C	^1H av	T_c, °C	^{13}C av
1a						4.90	−150[b]	95.2
1b						4.58	−115	92.8
1c	2.19	3.83	6.42	4.87	−115	4.66	−65	89.2
	37.9	37.9	142.0	111.9				
3[c]	2.10	4.27	6.00	5.00	−140	5.63[d]	−110[d]	103.8[d]
4[e]	3.39	4.40	5.98	5.19	−94	5.00	−10	97.3
	61.7	51.9	133.9	119.3				

[a] Chemical Shifts (δ) in ppm from TMS in THF-d_8 (unless otherwise noted). [b] Low-temperature spectrum recorded as the PPN$^+$ salt in a mixture of CHF_2Cl/CD_2Cl_2 (4:1).[13c] [c] **3** is $(\eta^3\text{-}C_7H_7)Co(CO)_3$, spectrum in CF_2Cl_2.[13b] [d] Hager, D., Edelmann, F., Takats, J., unpublished results. [e] **4** is the symmetrical isomer of $(\eta^3\text{-}C_7H_7)Os(CO)_3SnPh_3$, spectrum in CD_2Cl_2.[4c]

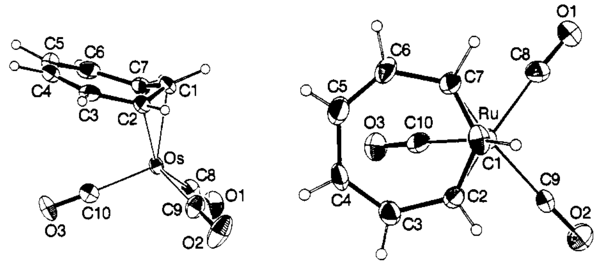

Figure 1. Perspective views of $(\eta^3\text{-}C_7H_7)M(CO)_3^-$ [**1b** (M = Ru), **1c** (M = Os)].

tions. The similarities in bonding between **1a–c** are vividly apparent from the table. Differences in bond lengths can mostly be accomodated by differences in metallic radii.[11]

The length of the C–O bond of the carbonyl ligands are almost identical. In the case of the Ru and Os complexes the CO ligand underneath the C_7H_7 ring has the marginally longer M–C bond. This in accord with its apical position in what can be described as quasi square-pyramidal geometry of the central metal atom. The η^3-enylic C–C bond lengths, at about 1.43 Å, are normal and very similar in all three cases. The other C–C bond distances are alternatively long and short. As expected the metal–carbon bond distance to the central carbon atom of the allylic fragment is shorter than the distances to the terminal positions,[12] in all three cases. The distances in the Ru and Os complexes are very similar. The ligand is hinged at the terminal allylic carbons into two planes with the interplanar angle being 37.2° for Os and 35.7° for Ru. The same angle for Fe is 31.3° which implies a decrease in conjugation between the allyl and diene fragments as one proceeds from Fe to Ru to Os. In unison with this, the two parts of the ligand (allyl and diene) are separated by longer bonds for Ru and Os (typically 1.46 Å) than for Fe (1.42 Å).

Fluxional Solution Behavior of Compounds 1. The variable-temperature ^1H NMR spectra of **1c** are shown in Figure 2. As can be seen, the single sharp line at room temperature broadens upon lowering the temperature and disappears into the base line at −65 °C. The low-temperature-limiting spectrum is reached at −110 °C, and at this stage the spectrum consists of four signals in the intensity ratio 2:2:2:1. The absolute assignment of the resonances was determined from H-H couplings obtained from resolution enhancement of the spectrum of **1c** at −115 °C. The peak of intensity 1 is clearly the central allylic hydrogen (H_1) and is split into a triplet by the neighboring H_2 protons with a coupling constant of 4.5 Hz. The H_2 signal is a doublet of doublets with coupling constants of 4.5 and 7.5 Hz to H_1 and H_3, respectively. As expected, H_3 is a complex multiplet, while H_4 has a doublet of doublets appearance with coupling constants of 8.3 (^3J) and 3.7 Hz (^4J) to H_3. The chemical shifts of the signals are clearly indicative of an η^3-bonding mode by comparison with the slow limiting NMR spectra of other known η^3-cycloheptatrienyl complexes.[13] As in **1c**, in the ^1H NMR spectra of these complexes the bound allylic hydrogens are typically at relatively high field, while the lowest field resonance is due to the outer diene positions (see Table

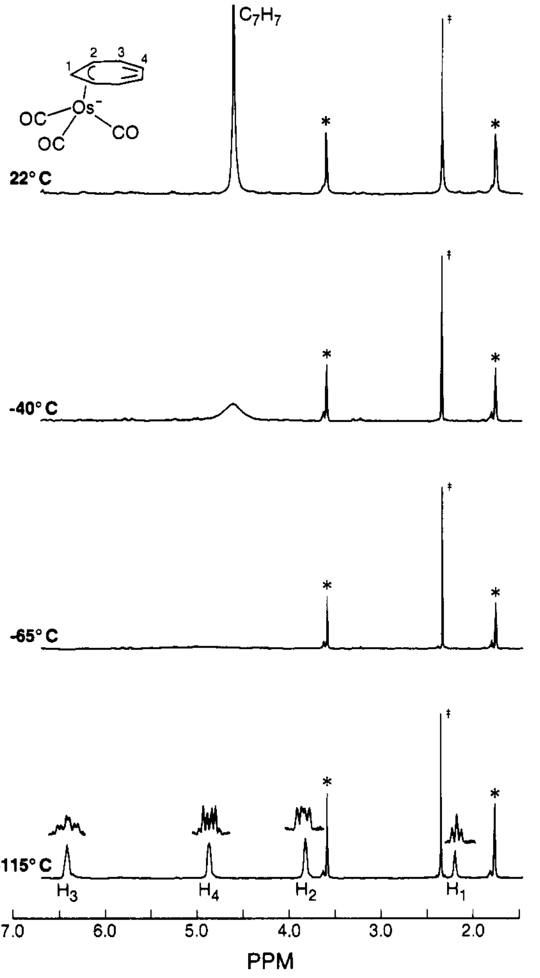

Figure 2. Variable-temperature ^1H NMR spectra of $[AsPh_4][(\eta^3\text{-}C_7H_7)Os(CO)_3]$ (**1c**) in THF-d_8 (the asterisk indicates residual THF and the dagger toluene solvate).

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[11] Wells, A. F. *Structural Inorganic Chemistry*, Clarendon Press: Oxford, 1975; p 1022. Note: the provided values of metallic radii differ from those of the covalent radii for Ru(0) and Os(0) (1.427 and 1.439 Å, respectively; see: Churchill, M. R.; Hollander, F. J.; Hutchinson, J. P. *Inorg. Chem.* **1977**, *16*, 2655). However, the difference between the two values is constant for both metals.

[12] Hsu, L.-Y.; Nordman, C. E.; Gibson, D. H.; Hsu, W.-L. *Organometallics* **1989**, *8*, 241.

[13] (a) Mann, B. E. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 3, p 132. (b) Bennett, M. A.; Bramley, R.; Watt, R. *J. Am. Chem. Soc.* **1969**, *91*, 3089. (c) Reuvers, R. G. A. Ph.D. Thesis, University of Alberta, 1978.

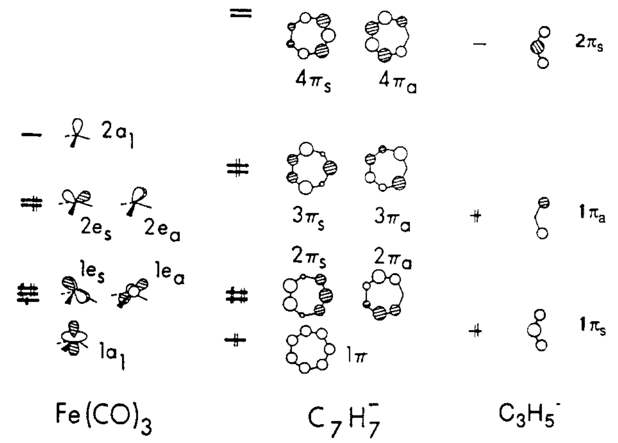

Figure 3. Schematic diagrams of the molecular orbitals of $Fe(CO)_3$ with $C_7H_7^-$ (D_{7h} symmetry), adapted from ref 8, and $C_3H_5^-$.

Table VI. ^{13}C NMR of Allylic Fragments Including η^3-C_7H_7[a]

compd[b]	C_1	C_2	ref
1c	37.9	37.9	this work
4	61.7	51.9	4c
5	144.0	52.8	14b
6	94.5	29.1	c
7	119.0	57.6	17
8	83.9	30.7	18
9	34.8	21.9	15

[a] Chemical shifts (δ) in ppm; spectrum in THF-d_8 (unless noted below). [b] **4** is the symmetrical isomer of (η^3-C_7H_7)$Os(CO)_3SnPh_3$, spectrum in CD_2Cl_2; **5** is KC_3H_5; **6** is (η^3-C_3H_5)$Os(CO)_3H$, spectrum in CD_2Cl_2; **7** is K(C_9H_9) (BCNT); spectrum in DME-d_{10}; **8** is $(BCNT)_2Fe$, spectrum in C_6D_6; **9** is $(P^iPr_3)_2Ni_2(\mu$-$C_3H_5)$, spectrum in toluene-d_8. [c] Kiel, G.-Y.; Takats, J. Unpublished results.

V). In the alternative η^4 structure one would expect the ^1H and ^{13}C resonances of the bound diene positions to be at much higher field.

In all cases studied so far, the mechanism of the fluxional process in η^3-cycloheptatrienyl complexes involves a series of 1,2-metal shifts around the seven-membered ring.[4a,13] The operation of the same mechanism in **1c** is given support by the slower broadening of the H_4 signal upon warming from −115 °C. Simulation of the spectra at different temperatures yielded an activation energy, ΔG^*, of 8.2 kcal mol^{-1} for this process in **1c**. It should be noted at this point that although the η^3- and η^4-bonding modes of the C_7H_7 ring are very close in energy and this has been used to account for the facile fluxionality of **1a**,[8] the 1,2-metal shift process does not require passage through the η^4-C_7H_7 form.[13]

The slow limiting spectrum for the Ru analogue was not obtained as it would have required considerably lower temperature than for **1c**. The variable-temperature ^1H NMR spectra of **1b** does, however, show considerable broadening of the cycloheptatrienyl ring signal with the coalescence temperature approached in THF at −100 °C. The ^1H NMR spectrum of **1a** shows rapid ring whizzing of the cycloheptatrienyl ring at −100 °C, although broadening of the single peak does occur below this temperature with the coalescence temperature reached at −150 °C.[13c]

The low-temperature ^{13}C NMR spectrum of **1c** is also recorded in Table V. At −100 °C, the ring signals are still not very sharp, and the resonances for C_1 and C_2 overlap because of the proximity of their chemical shifts.

Discussion

The solid-state structure of all three complexes conform to the (η^3-C_7H_7)$M(CO)_3^-$ bonding form A. In solution **1c** was also shown to exhibit this bonding fashion implying that complexes **1a** and **1b** are most likely to adopt this type of ligand bonding in solution as well. Thus, the reactivity difference and electrophilic discrimination of compounds **1** may not be related to the facility of the η^3 to η^4 interconversion, or the energy difference between the two forms, but to the variation in the metal to η^3-C_7H_7 ligand bonding as the transition metal is changed.

In order to easily visualize the relevant bonding interaction, the molecular orbitals of $Fe(CO)_3$ and C_7H_7 fragments, adapted from ref 8, together with the well-known molecular orbitals of the related allyl fragment are shown in Figure 3.

A clear difference between the allyl and η^3-C_7H_7 moieties is immediately apparent. For the allyl group, the $1\pi_a$ molecular orbital has the best energy match for interaction with the metal frontier orbitals. This ligand orbital has a node at the central allyl carbon atom. The situation with the η^3-C_7H_7 ligand is different. Although the degeneracy of the molecular orbital pairs of C_7H_7 under D_{7h} symmetry is lifted in compounds **1**, the energy difference between the two 3π molecular orbitals is not expected to be large, and consequently both will still be involved in the interaction with the $M(CO)_3$ fragment. Note that the $3\pi_s$ MO has significant amplitude at the central carbon of the η^3-C_7H_7 moiety. In accord with these considerations, the ^1H and ^{13}C signals of the central allyl atom resonate at the low field positions[14] (see Table VI). Substantial upfield shift in the position of these signals is seen only in dinuclear complexes containing bridging C_3H_5 moieties, where strong M $d\pi$ to $2\pi_s$ bonding is possible. A particularly striking example is the dinuclear Ni complex $(P^iPr_3)_2Ni_2(\mu$-$Cl)(\mu$-$C_3H_5)$[15] (**9**). On the other hand, in compounds containing the η^3-C_7H_7 unit, the central ^1H and ^{13}C signals are at high field because the HOMO's from the metal ($2e_s$, $2e_a$) and C_7H_7 ($3\pi_s$, $3\pi_a$) have substantial localization at the central atom (see Table VI). Consistent with this postulate, although perhaps somewhat surprisingly, calculations have shown that in **1a** more charge is localized on the ring in the η^3 mode (bonding form A) than in form B which features a "free" allyl anion.[8]

It is worth noting that the ^{13}C chemical shifts of carbanions have been related to π-electron density.[16] For instance, according to calculations, in KC_3H_5 (**5**) the central carbon of the allyl moiety has a π-electron density of 0.97, whereas the terminal carbons have a charge of 1.51 electrons,[16] with the larger density on the terminal carbons causing their upfield shift. The separation between the chemical shifts of the central and end carbons is 91 ppm (see Table VI). Although it is dangerous to make predictions concerning electron density on bound carbanionic ligands on the basis of their chemical shifts because of the well-known metal effect on ^{13}C chemical shifts,[14a] it is clear that the C_7H_7 ligand in **1c** carries a large amount of negative charge. As would be expected from such considerations, the chemical shifts of anionic **1c** are at higher field than in the neutral **4**. The identical chemical shifts of C_1 and C_2 in **1c** is also remarkable and corroborates our suggestion of important back-bonding to the central carbon as well.

Included in Table VI is the organic anion $BCNT^-$ (**7**)[17] and its iron complex $Fe(BCNT)_2$[18] (**8**). This anion con-

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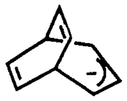
[14] (a) Mann, B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Chemists*; Academic Press: London, 1981. (b) O'Brien, D. H.; Russell, C. R.; Hart, A. J. *Tetrahedron Lett.* **1976**, 37.

[15] Hanko, R. *Agnew. Chem., Int. Ed. Engl.* **1985**, *24*, 704.

[16] O'Brien, D. H.; Hart, A. J.; Russell, C. R. *J. Am. Chem. Soc.* **1975**, *97*, 4410.

[17] Jonsall, G.; Ahlberg, P. *J. Chem. Soc., Perkin Trans. 2* **1987**, 461.



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tains an allylic fragment within a seven-membered ring, and while it is possible that there is some interaction involving the three unsaturated bridges,[17] the allylic portion is clearly more isolated than in cycloheptatrienyl complexes. This is reflected in the ^{13}C signals which resemble more closely the allyl anion.

Although the low-temperature-limiting spectra has not been attained for **1a** and **1b**, the averaged ^{13}C chemical shift of the ring carbons (**1a**, 95.2 ppm, **1b**, 92.8 ppm, **1c**, 89.0 ppm, all in THF-d_8) show a trend consistent with increased negative charge on the cycloheptatrienyl ligand in the order Fe < Ru < Os. These chemical shifts can be compared to the neutral complexes $(\eta^3\text{-}C_7H_7)M(CO)_2$(diphosphine)I (M = Mo, 105.3 ppm; M = W; 101.3 ppm).[19] These observations can best be explained by an increased metal π-basicity (toward the seven-membered ring) upon descending the metal triad. A second consequence of such an increase in back-bonding is the concomitant change to increased sp^3 character of the carbon atoms of the η^3-allylic unit. This effect is therefore also helpful in explaining the decreased conjugation between the bound allylic and unbound diene fragments of the C_7H_7 ring for Ru and Os and hence also the decreasing fluxional behavior which is observed upon descending the metal triad. These observations are also in accord with the apparent increase in basicity of the anionic complexes from Fe to Ru to Os. Indeed, while deprotonation of $(C_7H_8)M(CO)_3$ with KO^tBu occurs readily in THF (M = Fe, Ru, Os) at room temperature, upon cooling the solution to −78 °C the reverse reprotonation reaction occurs only for the Os anion. Of course, variations in metal π-basicities have also been used in explaining other well-known trends in organotransition-metal chemistry such as increased metal–ligand bond strengths,[20] olefin rotation barriers[21] down a triad, and the preference for classical over nonclassical hydrides[22] by electron-rich metals.

Summary

All three anionic complexes 1 contain an η^3-bonded cycloheptatrienyl ring as the ground-state structure in the solid state. A decrease in conjugation between the allylic portion of the ring and the free diene is observed for Ru and Os. For the Os complex, the same structure is adopted in solution as deduced from the slow limiting ^1H and ^{13}C NMR spectra. The slow limiting spectra could not be obtained for the Fe and Ru anions due to the higher rate of metal migration around the C_7H_7 ligand. In the osmium anion **1c**, probably as a result of more effective back-bonding to the ring, there is apparently more negative charge localized on the η^3-allyl fragment than in the Fe and Ru congeners. As a consequence, its reactivity toward electrophilic reagents is even more unpredictable than that of **1a** and **1b**.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and the University of Alberta for financial support of this work. Thanks are also due to G. Bigam for help with the resolution enhancement spectrum of **1c** and to Prof. R. E. D. McClung for use of the exchange simulation program.

Registry No. **1b**, 123857-58-9; **1b**·$0.5C_7H_8$, 123857-62-5; **1c**, 123857-59-0; **1c**·$0.5C_7H_8$, 123857-61-4; $(C_7H_8)Os(CO)_3$, 123857-60-3; $K(C_7H_7)Ru(CO)_3$, 119861-82-4.

Supplementary Material Available: Tables of anisotropic thermal parameters for non-hydrogen atoms and derived positional and thermal parameters for all atoms of **1b** and **1c** not mentioned in Tables II and III and complete listings of bond distances and angles for **1b** and **1c** (19 pages); listings of final observed and calculated structure factor amplitudes (21 pages). Ordering information is given on any current masthead page.

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