ORGANOMETALLICS

Actinide-to-transition metal bonds. Synthesis, characterization, and properties of metal-metal bonded systems having the tris(cyclopentadienyl)actinide fragment

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below −90 °C in toluene (<−130 °C in diethyl ether) solution substantial line broadening of the ^{1}H (400 MHz) and ^{13}C (100.6 MHz) NMR CH_2 resonances of **2** due to decreasing exchange rates is observed. However, for this compound both the intraligand syn/anti allyl hydrogen scrambling and intramolecular π-/σ-allyl exchange are taking place so rapidly that up to now **2** has eluded structural characterization on the basis of its "static" low-temperature-limiting NMR spectra.

The molecular structure of **2** was determined by X-ray diffraction at −173 °C.[6] The zirconium atom is coordinated to a η^5-cyclopentadienyl ligand and three differently bonded allyl groups arranged around the central metal in a pseudo tetrahedral geometry. One position is occupied by a σ-allyl group [Zr–C(7) = 2.375 (3) Å, C(7)–C(8) = 1.461 (5) Å, C(8)–C(9) = 1.332 (5) Å; Zr–C(7)–C(8) = 107.9 (2)°]. The remaining tetrahedral bonding sites are used to coordinate two η^3-allyl moieties. To a first approximation one of these appears to be an ordinary π-allyl ligand [C(4)–C(5) = 1.387 (5) Å, C(5)–C(6) = 1.382 (5) Å; C(4)–C(5)–C(6) = 123.9 (3)°] which is only slightly distorted by an "unsymmetrical" coordination to the Cp–Zr unit [C(4) positioned cis and the C(5)–C(6) vector positioned trans to Cp; Zr–C(4) = 2.405 (4) Å, Zr–C(5) = 2.525 (3) Å, Zr–C(6) = 2.549 (3) Å]. The bonding features of the η^3-allyl ligand "all-cis" to Cp are substantially different. Increasing zirconium-to-carbon distances [Zr–C(1) = 2.442 (4) Å, Zr–C(2) = 2.523 (3) Å, Zr–C(3) = 2.624 (3) Å] and decreasing carbon to carbon bond lengths [C(1)–C(2) = 1.412 (5) Å, C(2)–C(3) = 1.371 (6) Å] indicate a pronounced distortion toward an unsymmetrical σ,π-type (η^3-allyl)metal complex structure.[7] The observed hydrogen positions in the X-ray crystal structure analysis disclose additional systematic distortions of the η^3-allyl ligands. Relative to the C(4),C(5),C(6) plane the "meso" hydrogen H(5) is tilted substantially toward the zirconium center (0.24 (4) Å). This is not an uncommon structural feature for a (π-allyl)metal complex,[8] nor is the slight pyramidalization at C(4) (H(4)-syn coplanar, H(4)-anti turned away from the metal by 0.47 (4) Å). However, a substantial twisting at C(6) appears noteworthy. This distortion places H(6)-syn 0.15 (3) Å out of the allyl carbon plane toward the metal and places H(6)-anti by 0.34 (4) Å in the opposite direction. Similar effects are observed for the hydrogen atoms at the C(1), C(2), and C(3) of the allyl group (distortions: H(2), +0.19 (4) Å; H(1)-syn in plane; H(1)-anti, −0.43 (4) Å; H(3)-syn, +0.17 (3) Å; H(3)-anti, −0.30 (4) Å). In a formal way this type of an allyl ligand distortion observed in the solid-state structure of **2** might be regarded as modeling an intermediate stage along the reaction coordinate of the η^3–η^1 interconversion,[4] although this case is corresponding to a geometry being located rather close to the π-bonded isomer. This ground-state structural feature could possibly help to explain the extremely low activation barrier of the intramolecular allyl isomerization and interconversion. On the basis of the solid-state structure of **2** one might even speculate that the rearrangement of the three allyl ligands is not occurring independently but possibly in a "concerted" fashion.

Acknowledgment. Financial support from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged. We thank Dr. R. Benn and Dr. A. Rufinska for many low-temperature NMR spectra.

Supplementary Material Available: Tables of crystal data, atomic coordiniates, thermal parameters, and selected interatomic distances and angles for **2** (5 pages); a listing of observed and calculated structure factors for **2** (12 pages). Ordering information is given on any current masthead page.

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(6) Crystallographic data for **2**: $C_{14}H_{20}Zr$, M_r 279.5; crystal size 0.31 × 0.30 × 0.02 mm; orthorhombic, space group $P2_12_12_1$; a = 8.603 (3) Å, b = 18.520 (5) Å, c = 8.033 (4) Å; V = 1279.8 Å^3; Z = 4; T = −173 °C; d_{calcd} = 1.45 g cm^{-3}; graphite-monochromated Mo Kα radiation, λ = 0.710 69 Å; μ = 8.13 cm^{-1}; no absorption correction has been applied; hydrogen atoms were located in the difference fourier map and refined isotropically; all non-hydrogen atoms were refined anisotropically; the absolute configuration was determined by a Hamilton test of the R factor ratio of both enantiomers (significance $\alpha \gg 99.5$ %); Nonius CAD-4 (Ω–2θ scan technique with scan speeds varying from 1.0 to 10.0° min^{-1}, depending on the standard deviation to intensity ratio of a preliminary 10° min^{-1} scan; the time taken to measure the background was half that taken to measure the peak; Ω-scan range ($a + 0.35 \tan \theta$), where a was twice the average width of the Ω-scans of several low-angle reflections; horizontal detector aperture ($3.0 + 1.05 \tan \theta$) mm and vertical aperture 4.0 mm); reflections measured, 7894 ($\pm h,+k,+l$, $1° < \theta < 30°$); reflections unique, 3804 (R_{av} = 0.028); reflections observed, 3174 ($I \geqslant 2\sigma(I)$); number of variables, 216; R = 0.029, R_w = 0.028 ($w = 1/\sigma^2(F_o)$); goodness of fit, 1.16; maximum shift/error in the final cycle, 0.1; final difference Fourier, 0.78 e Å^{-3} (close to Zr).

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Actinide-to-Transition Metal Bonds. Synthesis, Characterization, and Properties of Metal–Metal Bonded Systems Having the Tris(cyclopentadienyl)actinide Fragment

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Summary: Reaction of Cp_3AnCl complexes (Cp = η^5-C_5H_5; An = Th, U) and $(CH_3C_5H_4)_3ThCl$ with $CpM(CO)_2Na$ (M = Fe, Ru) yields the corresponding metal–metal bonded compounds Cp_3An–$M(Cp)(CO)_2$ and $(CH_3C_5H_4)_3Th$–$M(Cp)(CO)_2$. Electron-releasing tendencies follow the order Cp_3U– > Cp_3Th– ≫ $[(CH_3)_5C_5]_2Th(X)$– (X = Cl, I, CH_3). Evidence for hindered rotation about the metal–metal bonds and facile cleavage by alcohols and ketones is presented.

We recently described[1] the synthesis and properties of $Cp'_2Th(X)Ru(Cp)(CO)_2$ complexes (Cp′ = η^5-$(CH_3)_5C_5$; Cp = η^5-C_5H_5; X = Cl, I, CH_3) which contain unsupported actinide-to-transition metal bonds.[2-4] The scope of ac-

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(1) (a) Sternal, R. S.; Brock, C. P.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8270–8272. (b) Sternal, R. S.; Kanatzidis, M. G.; Brock, C. P.; Marks, T. J., submitted for publication.

(2) For molecular orbital calculations, see: Bursten, B. E.; Novo-Gradac, K. J. *J. Am. Chem. Soc.* **1987**, *109*, 904–905.

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Table I. Comparative Infrared Spectral Data for Complexes with Actinite-to-Transition Metal Bonds[a]

compound	ν_{CO}, cm^{-1}	
	toluene soln	Nujol mull
$Cp_3ThFe(Cp)(CO)_2$ (**1**)	1927, 1873	1918, 1855
$Cp_3ThRu(Cp)(CO)_2$ (**2**)	1949, 1886	1939, 1868
$Cp_3UFe(Cp)(CO)_2$ (**3**)	1921, 1869	1915, 1847
$Cp_3URu(Cp)(CO)_2$ (**4**)	1944, 1882	1935, 1864
$(MeC_5H_4)_3ThFe(Cp)(CO)_2$ (**5**)	1927, 1871	1918, 1854
$(MeC_5H_4)_3ThRu(Cp)(CO)_2$ (**6**)	1947, 1885	1936, 1869
$Cp'_2Th(Cl)Ru(Cp)(CO)_2$	1971, 1910	1967, 1893
$Cp'_2Th(I)Ru(Cp)(CO)_2$	1972, 1911	1968, 1900
$Cp'_2Th(CH_3)Ru(Cp)(CO)_2$	1962, 1897	1958, 1891
$CpRu(CO)_2I$	2055, 2007[b]	
$CpRu(CO)_2H$	2033, 1973[b]	
$CpRu(CO)_2Ge(CH_3)_3$	2009, 1954[c]	
$Cp_2Zr(CH_3)Ru(Cp)(CO)_2$		1950, 1880[d]
$Cp_2Zr(CH_3)Fe(Cp)(CO)_2$		1937, 1872[d]

[a] Spectra at Northwestern were recorded on a Nicolet 7199 FT-IR spectrometer and are considered accurate to ±1.0 cm^{-1}. [b] Reference 18; CS_2 solution. [c] Sosinsky, B. A.; Knox, S. A. R.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1975**, 1633–1640; hexane solution. [d] Reference 13.

tinide–transition metal bonding is of great interest in these studies, and we now report an elaboration of such chemistry based upon the Cp_3An– fragment (An = Th, U). Taken together, the two systems provide a perspective on the transmission of metal/ligand electronic effects through, and conformational energetics about, this unusual type of metal–metal bond, as well as evidence for high reactivity.

The reaction of thorium and uranium Cp_3AnCl complexes[5] with $CpM(CO)_2Na$ reagents (M = Fe,[6] Ru[7]) in THF yields, after solvent evaporation and recrystallization from THF/pentane (by diffusion), the corresponding extremely air-sensitive $Cp_3AnM(Cp)(CO)_2$ complexes **1**–**4** (eq 1). In

$$Cp_3AnCl + CpM(CO)_2Na \xrightarrow[25\ °C,\ 2\ h]{THF} \underset{\mathbf{1-4}}{Cp_3AnM(Cp)(CO)_2} + NaCl \quad (1)$$

1, An = Th, M = Fe, yellow microcrystals, 65% isolated yield

2, An = Th, M = Ru, colorless microcrystals, 73% isolated yield

3, An = U, M = Fe, brown solid, 72% isolated yield

4, An = U, M = Ru, yellow-brown microcrystals, 61% isolated yield

a similar manner, tris(methylcyclopentadienyl) complexes can also be prepared (eq 2). These new compounds have

$$(MeC_5H_4)_3ThCl^8 + CpM(CO)_2Na \xrightarrow[25\ °C,\ 2\ h]{THF} \underset{\mathbf{5,\ 6}}{(MeC_5H_4)_3ThM(Cp)(CO)_2} + NaCl \quad (2)$$

5, M = Fe, pale yellow microcrystals, 85% isolated yield

6, M = Ru, colorless microcrystals, 70% isolated yield

been characterized by standard analytical/spectroscopic techniques,[9] and compound **1** has also been characterized by X-ray diffraction (Fe–Th = 2.940 (5) Å).[10]

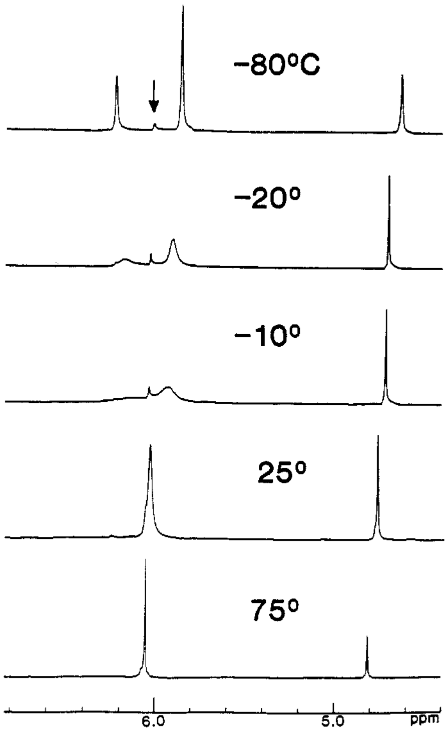

Figure 1. Variable-temperature, 270-MHz ^1H NMR spectra of a solution of $Cp_3ThRu(Cp)(CO)_2$ (**2**) in toluene-d_8. The arrow indicates an impurity.

Structurally diagnostic ν_{CO} infrared spectral data for **1**–**6** and related compounds[11] are set out in Table I. The

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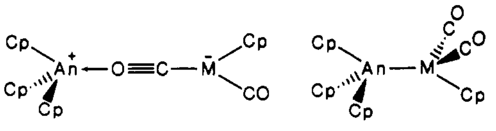
(9) (a) **1**: ^1H NMR (C_6D_6) δ 6.06 (s, 15 H, Cp_3Th), 4.25 (s, 5 H, CpFe); $^{13}C\{^1H\}$ NMR (THF-d_8) δ 220.2 (CO), 117.9 (Cp_3Th), (83.96 (CpFe); mass spectrum (15 eV), *m/e* (relative abundance, assignment) 604 (0.7, $Cp_3ThFeCp(CO)_2^+$), 427 (100, Cp_3Th^+). Anal. Calcd for $C_{22}H_{20}O_2FeTh$: C, 43.73; H, 3.34. Found: C, 44.71; H, 3.63. This compound consistently gave C analyses which were ca. 1% high. (b) **2**: ^1H NMR (C_6D_6) δ 6.08 (s, 15 H, Cp_3Th), 4.77 (s, 5 H, CpRu); $^{13}C\{^1H\}$ NMR (THF-d_8) δ 209.5 (CO), 117.5 (Cp_3Th), 87.3 (CpRu); mass spectrum (15 eV), *m/e* (relative abundance, assignment) 650 (0.4, $Cp_3ThRuCp(CO)_2^+$), 427 (100, Cp_3Th^+). Anal. Calcd for $C_{22}H_{20}O_2RuTh$: C, 40.68; H, 3.10. Found: C, 41.06; H, 2.84. (c) **3**: ^1H NMR (C_6D_6) δ –5.60 (br s, 15 H, Cp_3U), –12.82 (s, 5 H, CpFe); $^{13}C\{^1H\}$ NMR (THF-d_8) δ 272.5 (CO), 89.64 (CpFe), the Cp_3U signal was not observed; mass spectrum (15 eV), *m/e* (relative abundance, assignment) 433 (100, Cp_3U^+). Anal. Calcd for $C_{22}H_{20}O_2FeU$: C, 43.30; H, 3.30. Found: C, 43.44; H, 3.52. (d) **4**: ^1H NMR (C_6D_6) δ –5.26 (br s, 15 H, Cp_3U), –10.56 (s, 5 H, CpRu); mass spectrum (15 eV), *m/e* (relative abundance, assignment) 656 (0.2, $Cp_3URuCp(CO)_2^+$), 433 (100, Cp_3U^+), 368 (20, Cp_2U^+). Anal. Calcd for $C_{22}H_{20}O_2RuU$: C, 40.31; H, 3.08. Found: C, 40.28; H, 3.12. (e) **5**: ^1H NMR (C_6D_6, 65 °C) δ 6.02 (s, 12 H, $Th(C_5H_4CH_3)_3$), 4.39 (s, 5 H, CpFe), 2.21 (s, 9 H, $Th(C_5H_4CH_3)_3$); $^{13}C\{^1H\}$ NMR (C_6D_6, 65 °C) δ 219.8 (CO), 119.9, 117.1 ($Th(C_4H_4CCH_3)_3$), 83.20 (CpFe), 15.76 (CH_3); the ThCp ring carbon atom bonded to the CH_3 group was not observed; mass spectrum (15 eV), *m/e* (relative abundance, assignment) 469 (100, $(MeC_5H_4)_3Th^+$). Anal. Calcd for $C_{25}H_{26}O_2FeTh$: C, 46.45; H, 4.05. Found: C, 46.45; H, 4.17. (f) **6**: ^1H NMR (C_6D_6) δ 6.04, 5.99 (br d, 12 H, $Th(C_5H_4CH_3)_3$), 4.83 (s, 5 H, CpRu), 2.19 (s, 9 H, $Th(C_5H_4CH_3)_3$); $^{13}C\{^1H\}$ NMR (C_6D_6, 65 °C) δ 209.1 (CO), 119.5, 116.6 ($Th(C_4H_4CCH_3)_3$), 86.55 (CpRu), 15.70 (CH_3), the Th Cp ring carbon atom bonded to the CH_3 group was not observed; mass spectrum (15 eV), *m/e* (relative abundance, assignment) 692 (13, $(MeC_5H_4)_3ThRuCp(CO)_2^+$), 469 (100, $(MeC_5H_4)_3Th^+$). Anal. Calcd for $C_{25}H_{26}O_2RuTh$: C, 43.42; H, 3.79. Found: C, 43.20; H, 3.89.

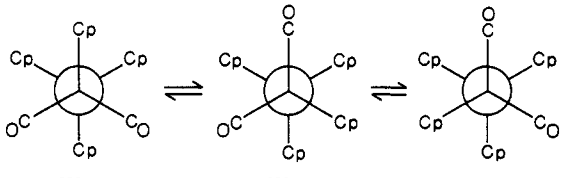
(10) Sternal, R. S.; Sabat, M.; Marks, T. J., unpublished results. This compound crystallizes in the orthorhombic space group *Fmmm* with a = 24.445 (8) Å, b = 24.846 (6) Å, c = 13.748 (3) Å, and Z = 16. Structure refinement is in progress, and a full report will be sumitted shortly.

importance of contributing isocarbonyl structures (I)[12] can be immediately ruled out either in solution or in the solid state. Instead, the metal–metal bonded structure II is in good accord with ν_{CO}, diffraction,[10] and NMR (vide infra) data for all compounds. Trends in the ν_{CO} data indicate that the actinide fragments transfer an appreciable amount of electron density onto the $CpM(CO)_2$ groups. This trend is in accord with a relatively polar[2] metal–metal bonding description. Comparisons of the $Cp'_2Th(X)Ru(Cp)(CO)_2$ data to those for **2** and **6** also reveal a substantial actinide ligation effect that is transmitted through the metal–metal bond: the Cp_3An fragment is less electron-withdrawing. In addition, the **1**/**3**,**2**/**4** data reveal a small but real actinide effect: thorium is more electron-withdrawing than uranium. That this effect is independent of transition metal argues that it is electronic rather than steric in origin. The ν_{CO} data also reveal that $Cp'_2Th(X)$– is slightly more electron-withdrawing than $Cp_2Zr(X)$–.[13]



I II

Variable-temperature ^1H NMR data for **1**–**6** (e.g., Figure 1) are consistent with staggered conformations and hindered rotation about the metal–metal bonds in solution (IIIa–c).[14] A simple two-site kinetic analysis appropriate for unequal populations[15] yields the activation parameters compiled in Table II. Interestingly, the free energies of activation are rather insensitive to metal identity and hence to metal–metal distance. The barriers are comparable to those for alkyl group rotation in Cp_3AnR[16] complexes and for rotations about a number of other metal–metal single bonds.[17]



IIIa IIIb IIIc

Table II. Kinetic Data for Dynamic Processes in Metal-Metal Bonded Organoactinides

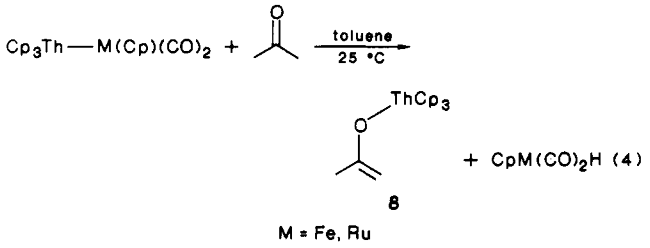
compound	T_c,[a] K	$\Delta\nu$,[b] Hz	$\Delta G^*(T_c)$,[c] kcal/mol
$Cp_3ThFe(Cp)(CO)_2$ (**1**)	278	91.66	13.5 (7)
$Cp_3ThRu(Cp)(CO)_2$ (**2**)	263	99.58	12.7 (7)
$Cp_3UFe(Cp)(CO)_2$ (**3**)	303	550.5	13.7 (7)
$Cp_3URu(Cp)(CO)_2$ (**4**)	318	601.2	14.4 (7)
$(MeC_5H_4)_3ThFe(Cp)(CO)_2$ (**5**)	238	36.92	11.9 (7)
$(MeC_5H_4)_3ThRu(Cp)(CO)_2$ (**6**)	238	30.33	12.0 (7)

[a] Coalescence temperature. [b] Frequency difference at slow exchange. [c] Average of ΔG^*'s for the two unequally populated sites.

Preliminary experiments indicate that the present actinide-to-transition metal bonds react rapidly with polar reagents. Thus, alcoholysis is rapid and quantitative by NMR (eq 3) to yield the corresponding $CpM(CO)_2H$ complexes[18] (identified by NMR) and the known thorium alkoxide **7**.[19] More interestingly, complexes **1** and **2** react rapidly and quantitatively (by NMR) with acetone to yield the corresponding transition-metal hydrides (identified by NMR) and thorium enolate **8**[20] (eq 4).

$$Cp_3Th\text{–}M(Cp)(CO)_2 + CF_3CH_2OH \xrightarrow[25\ °C]{toluene} \underset{\mathbf{7}}{Cp_3ThOCH_2CF_3} + CpM(CO)_2H \quad (3)$$

$$M = Fe, Ru$$



These results expand the number of known systems with actinide-to-transition metal bonds and provide the first information on the transmission of actinide and actinide ligation characteristics through such bonds. Further work will focus on thermochemistry and unusual reactivity patterns.

Acknowledgment. We are grateful to NSF for support of this research under Grant CHE8306255.

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(11) Solutions for infrared spectroscopy were prepared in a glovebox using toluene distilled from Na/K alloy. Single-crystal NaCl cells were fitted with O-ring-sealed caps. Prior to spectroscopy, the cells, O-rings, and caps were dried under high vaccum at 60 °C for 12 h and then flushed with three fillings of sample solution. Without such precautions, hydrolysis of these extremely sensitive complexes occurs to produce the corresponding $CpM(CO)_2H$ compound. Infrared solutions in ref 1a were contaminated with this byproduct.

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(20) (a) **8**: ^1H NMR (C_6D_6) δ 6.15 (s, 15 H, Cp_3Th), 4.09 (s, 1 H, CH_2), 3.95 (s, 1 H, CH_2), 1.74 (s, 3 H, CH_3). ^{13}C NMR (C_6D_6) δ 165.4 (s, CO), 117.9 (d, J_{C-H} = 166 Hz, Cp_3Th), 86.97 (t, J_{C-H} = 156 Hz, CH_2), 22.62 (q, J_{C-H} = 128 Hz, CH_3); IR (Nujol, ν_{CO}, cm^{-1}) 3097 w, 3080 w, 1639 m, 1602 m, 1438 m, 1274 s, 1152 w, 1068 w, 1034 s, 1008 s, 991 m, 874 m, 776 s, 502 w, 476 m; mass spectrum (70 eV), *m*/*e* (relative abundance, assignment) 484 (21, $Cp_3ThOC(CH_2)(CH_3)^+$), 427 (15, Cp_3Th^+), 419 (100, $Cp_2Th\text{–}OC(CH_2)(CH_3)$), 377 (19, $Cp_2ThCH_3^+$), 362 (20, Cp_2Th^+), 313 (85, $CpThO^+$). Anal. Calcd for $C_{18}H_{20}OTh$: C, 44.63; H, 4.16. Found: C, 44.64; H, 4.09. (b) Such complexes have previously been prepared by carbonylation routes: Sonnenberger, D. C.; Mintz, E. A.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 3484–3491.