reverse trend, as discussed previously,[16] but the larger changes in K_{ads} determine the overall trend.

Also, the increasing order of HDS reactivities of methyl-substituted thiophenes, T (1.0) < 2-MeT (1.5) < 3-MeT (1.9) < 2,5-Me_2T (2.0),[7] on Co-Mo/Al_2O_3 follows the trend expected from the adsorption equilibrium constants (K_{ads}). It is likely[22] that the reactivity order of the adsorbed thiophenes follows the opposite trend with the more methyl-substituted thiophenes undergoing slower desulfurization. But here, as for deuterium exchange, larger differences in K_{ads} than in k would explain the overall trend in reactivity.

In conclusion, the K' values for reaction 2 support η^5-bonded thiophene as the form of adsorption on HDS catalysts and also reasonably account for trends in the deuterium exchange and HDS reactivity of methyl-substituted thiophenes on HDS catalysts.

Acknowledgment. We thank Johnson Matthey, Inc., for a generous loan of $RuCl_3$.

Registry No. T, 110-02-1; DBT, 132-65-0; 2-MeT, 554-14-3; 3-MeT, 616-44-4; 2,3-Me_2T, 632-16-6; 2,5-Me_2T, 638-02-8; 2,3,4-Me_3T, 1795-04-6; 2,3,5-Me_3T, 1795-05-7; Me_4T, 14503-51-6; [CpRu(T)]PF_6, 107799-36-0; [CpRu(2-MeT)]PF_6, 107799-43-9; [CpRu(3-MeT)]PF_6, 117094-83-4; [CpRu(2,3-Me_2T)]PF_6, 117094-84-5; [CpRu(2,5-Me_2T)]PF_6, 114571-22-1; [CpRu(2,3,4-Me_3T)]PF_6, 117094-86-7; [CpRu(2,3,5-Me_3T)]PF_6, 117094-87-8; [CpRu(Me_4T)]PF_6, 117094-89-0; [CpRu(BT)]PF_6, 112068-98-1; [CpRu(DBT)]PF_6, 117094-91-4; [CpRu(CH_3CN)$_3$]PF_6, 80049-61-2.

Addition of Sc–H, Sc–C, and Sc–N Bonds to Coordinated Carbon Monoxide. Structure of a Methylscandoxycarbene Derivative of Cobalt[1]

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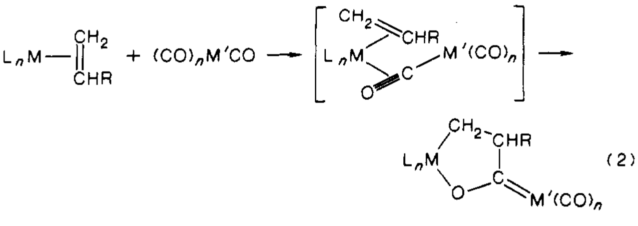
$Cp*_2ScR$ ($Cp* = \eta^5-C_5Me_5$; R = H, CH_3) react with Cp_2MCO ($Cp = \eta^5-C_5H_5$, M = Mo, W) to give the corresponding R-substituted scandoxycarbenes $Cp_2M{=}C(R)OScCp*_2$. Similarly, $Cp*_2ScR$ (R = H, CH_3, CH_2CH_2Ph, NMe_2) react with $CpM(CO)_2$ (M = Co, Rh) to afford the R-substituted scandoxycarbenes. The structure of $CpCo(\mu_2,\eta^1,\eta^1-CO)\{{=}C(CH_3)OScCp*_2\}$ has been determined by a single-crystal X-ray diffraction methods, revealing a $\mu_2,\eta^1\eta^1$-carbonyl ligand in addition to the scandoxycarbene moiety bridging the Sc and Co atoms. $CpCo(\mu_2,\eta^1,\eta^1-Co)\{{=}C(CH_3)OScCp*_2\}$ crystallizes in space group $P\bar{1}$ (a = 8.592 (4) Å, b = 10.923 (2) Å, c = 14.648 (2) Å; α = 91.074 (14)°, β = 100.84 (2)°, γ = 100.77 (3)°; Z = 2). Least-squares refinement led to a value for R of 0.046 ($I > 3\sigma$) and a goodness of fit of 3.51 for 4593 reflections.

Introduction

Despite the extensive chemistry which has been developed for "Fischer carbene" complexes, the original synthesis, with slight variations, has remained the principal route into this important class of compounds[2] (eq 1). While this method has been used to prepare a wide range of derivatives, relatively few carbene complexes of cobalt have been synthesized by this route.[3]

$$L_nMC{\equiv}O + LiR \rightarrow L_nM{=}C(OLi)R \xrightarrow[-LiX]{R'X} L_nM{=}C(OR')R \quad (1)$$

Several reports of novel routes into this class of compounds have recently appeared. Lappert and others have utilized electron-rich olefins to synthesize bis(amine)-substituted carbenes.[4] Erker[5] has utilized olefin complexes of the group 4 transition metals to effect the synthesis of metallacyclic carbenes from metal carbonyls, including those of cobalt, likely via a concerted electrocyclic ring closure (eq 2). Recently Mashima[6] has used this strategy to prepare exocyclic titanoxycarbenes of Cr, Mo, W, and Re. Reactions of metal carbonyls with titanium or aluminum amides to yield NMe_2-substituted "titanoxy" or "alumoxy" carbenes have been reported by Petz.[7] Earlier work from these laboratories demonstrated that $Cp*_2ZrH_2$ and $Cp*_2ZrHX$ are effective reagents for converting metal carbonyls to hydrogen-substituted "zirconoxycarbenes",[8] $L_nM{=}C(H)OZrXCp*_2$ (X = H, halide).



All of these methods lack generality and are apparently specific in affording exocyclic, NR_2 or H-substituted carbenes. We report herein that $Cp*_2ScR$ (R = H, alkyl, amide) is an effective and more general reagent for the synthesis of hydride-, alkyl-, or amide-substituted "scandoxycarbene" complexes from carbonyls of the type

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[†] Contribution no. 7735.

(1) Part of this work was previously presented at the 192nd National Meeting of the American Chemical Society in Anaheim, CA, Sept 1986.

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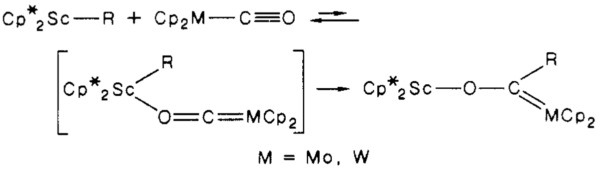
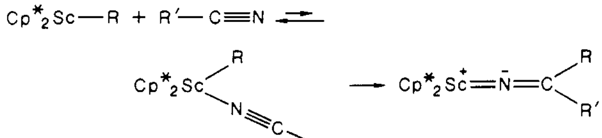
$CpM(CO)_2$ (Cp = η^5-C_5H_5; M = Co, Rh). Cp^*_2ScR (R = H, CH_3) also reacts with the more sterically encumbered Cp_2MCO (M = Mo, W) to give the corresponding H- and CH_3-substituted scandoxycarbenes. The versatility of Cp^*_2ScR in effecting these transformations can be attributed to the strongly Lewis acidic nature of the Sc center, which activates the carbonyl toward intramolecular nucleophilic attack by R. The structure of a representative example, $CpCo(\mu_2\text{-}CO)\{{=}C(R)OScCp^*_2\}$, has been determined by X-ray diffraction methods.

Results and Discussion

Reactivity of Cp^*_2ScR with Cp_2MCO (R = H, CH_3, C_6H_5, $CH_2CH_2C_6H_5$, $N(CH_3)_2$; M = Mo, W). Both $Cp^*_2ScH(THF)$ and $Cp^*_2ScCH_3$[9] react with Cp_2MCO at 25 °C to give $Cp_2M{=}C(R)OScCp^*_2$ in 50–60% yield. No intermediates are observed by NMR during the course of the reaction. On the other hand, when Cp_2WCO is treated with Cp^*_2ScCl, an adduct is formed with $\nu(CO) = 1835\ cm^{-1}$, 70 cm^{-1} lower than $\nu(CO)$ of Cp_2WCO, indicative of a Lewis acid–base interaction between the highly electrophilic scandium center and the carbonyl oxygen, analogous to the interaction between $AlCl_3$ and metal carbonyl.[10] Presumably, the reaction of the hydride and methyl compounds also proceed by initial adduct formation with polarization of the CO bond, followed by intramolecular nucleophilic attack by the scandium subsitutent (eq 3).


(3)

This sequence resembles the reaction of Cp^*_2ScR with cyanides, for which initial N-coordination of the nitrile is followed by a 1,3-alkyl shift to give azomethine complexes.[11]


(4)

The ^1H NMR spectra and color of these scandoxycarbenes $Cp_2M{=}C(CH_3)OScCp^*_2$ (M = Mo, W) are very similar to those for the zirconoxycarbenes of molybdenocene and tungstenocene, $Cp_2M{=}C(H)OZr(X)Cp^*_2$ (M = Mo, W), reported earlier.[8] Particularly characteristic is the inequivalence of the η^5-C_5H_5 ligands, indicating that the carbene substituents $[OScCp^*_2]$ and $[CH_3]$ or [H] point toward the cyclopentadienyl rings of the bent metallocene. π-Bonding between the carbene carbon and the transition metal dictates this sterically least favorable orientation. Steric interactions with the cyclopentadienyl ligands apparently limit the size of groups which may be added to the Cp_2MCO system. Thus, $Cp^*_2ScCH_2CH_2C_6H_5$, $Cp^*_2ScN(CH_3)_2$, and $Cp^*_2ScC_6H_5$ show no reactivity toward Cp_2MCO (M = Mo, W) even at elevated temperatures. Both $Cp^*_2Zr(CH_3)_2$ and $Cp_2Zr(CH_3)_2$ fail to react with Cp_2MCO at 80 °C. In the latter case it is not clear whether steric effects or the large Zr–CH_3 bond dissociation energy predominates.[12]

The scandoxycarbene complexes, when heated in benzene for days at 80 °C, slowly decompose to unidentified products. However, when heated to 80 °C under H_2, $Cp_2W{=}C(CH_3)OScCp^*_2$ is cleanly converted to $Cp_2W{=}C(H)OScCp^*_2$ and CH_4 (eq 5). The possibility that reaction 3 is reversible was therefore addressed by examining the reactivity of $Cp_2W{=}C(CH_3)OScCp^*_2$ with $Cp^*_2ScCD_3$ (eq 6). Only $Cp^*_2ScCD_3$ is observed in the ^2H NMR (δ 0.15) spectrum of this mixture at room temperature; however, after several minutes at 80 °C a peak at δ 2.08 corresponding to $Cp_2W{=}C(CD_3)OScCp^*_2$ appears, indicative of a dynamic equilibrium between Cp_2WCO, $Cp^*_2ScCH_3$, and $Cp_2W{=}C(CH_3)OScCp^*_2$. Considering equilibrium (6) and the very high reactivity of $Cp^*_2ScCH_3$ with dihydrogen,[9] the mechanism of conversion of $Cp_2W{=}C(CH_3)OScCp^*_2$ and dihydrogen to $Cp_2W{=}C(H)OScCp^*_2$ and methane is readily apparent: the $Cp^*_2ScCH_3$ from equilibrium (6) is converted to CH_4 and Cp^*_2ScH, which subsequently reacts rapidly with Cp_2WCO to form $Cp_2W{=}C(H)OScCp^*_2$.

$$Cp_2W{=}C(CH_3)OScCp^*_2 + H_2 \xrightarrow{80\ °C} Cp_2W{=}C(H)OScCp^*_2 + CH_4 \quad (5)$$

$$Cp^*_2ScCD_3 + Cp_2W{=}C(CH_3)OScCp^*_2 \rightleftharpoons Cp^*_2ScCH_3 + Cp_2W{=}C(CD_3)OScCp^*_2 \quad (6)$$

Attempts to replace the scandoxycarbene ligand with other functional groups were unsuccessful. No reaction is observed between $Cp_2M{=}C(R)OScCp^*_2$ and $HN(CH_3)_2$, despite the fact that this is a common route to convert Fischer-type carbenes to analogous substituted amine derivatives.[13] Treatment with methanol leads instead to cleavage of a Sc–(η^5-C_5Me_5) bond and subsequent decomposition.

Reactivity of Cp^*_2ScR (R = H, CH_3, $CH_2CH_2C_6H_5$, $CH(SiCH_3)_2$, C_6H_5, $CC(CH_3)$, $N(CH_3)_2$) with $CpM(CO)_2$ (M = Co, Rh). Earlier work by Barger[14] has shown that when $CpM(CO)_2$ (M = Co, Rh) are treated with Cp^*_2ZrHX (X = H, Cl, F), two possible pathways may be followed, dpending upon the nature of X. When X = H, elimination of H_2 occurs, and a metal–metal bonded species with a bridging and semibridging carbonyl is formed. A possible intermediate is observed in this reaction (M = Rh), which is believed to be a zirconoxycarbene. When X = Cl or F, the products are the chloro- or fluoro-substituted zirconoxycarbenes.

Since reductive elimination of RH (R = H, alkyl, etc.) is unavailable in the Cp^*_2ScR system, the reactivity observed is similar to that seen for Cp^*_2ZrHX (X = Cl or F). Moreover, a variety of Cp^*_2ScR complexes (R = H, CH_3, $CH_2CH_2C_6H_5$, $N(CH_3)_2$) react quickly and cleanly with $CpM(CO)_2$ to give the R-substituted scandoxycarbene products in good yield (50–70%) (eq 7). These sterically much less encumbered monocyclopentadienyl systems do

$$Cp^*_2ScR + CpM(CO)_2 \rightarrow Cp(CO)M{=}C(R)OScCp^*_2 \quad (7)$$

R = $H, CH_3, CH_2CH_2C_6H_5, NMe_2$, M = Co;
R = H, CH_3, M = Rh

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Table I. Structural Characteristics of Compounds Containing μ_2,η^1,η^1-CO Ligands

	M-C-O (deg)	M-O-C (deg)	d(C-O) (Å)	ν(CO) (cm^{-1})	ref
$Cp(CO)_2Mo-CO-Ti(THF)Cp_2$	178.0	135.4	1.201	1650	27
$Cp(CO)_2Mo-CO-Ti(CH_3)Cp_2$	178.8	144.3	1.212	1623	28
$Cp(CO)_2Mo-CO-Zr(CH_3)Cp_2$	178.2	145.5	1.236	1545	29
$(CO)_3Co-CO-Yb(THF)Cp^*_2$	177.8	163.0	1.188	1798, 1761	30
$(Cp(CO)_2Mo-CO-)_2ZrCp^*_2$	177.8	170.7	1.217	1578, 1533	31
$Cp(CO)_2(C(CH_3)O)Mo-CO-Zr(CH_3)Cp_2$	172.3	77.6	1.241	1600	17b
$Cp(\mu\text{-}C(CH_3)O-)Co-CO-ScCp^*_2$	169.9	110.9	1.268	1795	this work

not as severely constrain the type of R group which may be added. Once again, however, neither $Cp^*_2Zr(CH_3)_2$ nor $Cp_2Zr(CH_3)_2$ react, suggesting that the higher Lewis acidities of the Cp^*_2ScR derivatives are the main factor responsible for the facility of the addition of Sc–C bonds to coordinated carbon monoxide.

Interestingly, even when β-H elimination is available, as in the phenethylscandium derivative, simple addition of the intact $[CH_2CH_2C_6H_5]$ substituent to a carbonyl of $CpCo(CO)_2$ occurs. By contrast, addition of 2-butyne to a variety of alkyl complexes of the type $Cp^*_2ScCH_2CH_2R$ (including $Cp^*_2ScCH_2CH_2C_6H_5$) invariably results in β-H elimination of $CH_2{=}CHR$ and subsequent formation of $Cp^*_2ScC(CH_3){=}C(CH_3)H$.[15a]

With bulkier alkyl substituents such as $CH\{Si(CH_3)_3\}_2$, no reaction of Cp^*_2ScR with $CpM(CO)_2$ (M = Co, Rh) occurs, even at 80 °C. No reaction is observed with $Cp^*_2ScC_6H_5$ or $Cp^*_2ScC{\equiv}CCH_3$; however, in these cases, the strong Sc–C bonds are probably the cause of their lower reactivities.[12]

While the spectroscopic features of the scandoxycarbene ligands of cobalt and rhodium complexes are consistent with their formulation, a low-frequency CO stretch at approximately 1800 cm^{-1} is apparent in their infrared spectra, suggesting some type of interaction of the remaining carbonyl with the coordinatively unsaturated Sc center. Moreover, ^{13}C NMR spectra for $Cp(CO)Rh{=}C(CH_3)OScCp_2$ exhibit two downfield resonances with rather different Rh–^{13}C coupling constants (δ 206.7 (J_{Rh-C} = 114) Hz) and δ 279.1 (J_{Rh-C} = 56 Hz); cf. $Cp(CO)RhCN(CH_3)CH_2CH_2NCH_3$ δ 196.84 (J_{Rh-C} = 92.9 Hz) and δ 207.72 (J_{Rh-C} = 62.9 Hz).[4a]

In order to clarify the nature of this interaction, a single-crystal X-ray diffraction study of $CpCo(\mu_2,\eta^1,\eta^1\text{-}CO)\{{=}C(CH_3)OScCp^*_2\}$ was carried out. The molecular structure is shown in Figure 1, and a skeletal view is shown in Figure 2. As is readily apparent, the low ν(CO) and the additional downfield ^{13}C NMR shift are attributable to the μ_2,η^1,η^1 carbonyl. Whereas O2 is obviously bonded to the Sc (d(Sc–O2) = 2.331 (2)Å), C2 is beyond a reasonable bonding distance (d(Sc–C$_2$) = 2.979 (4) Å). By contrast, the μ_2,η^1,η^2 carbonyl for $(\eta^5\text{-}C_5H_5)Co(\mu\text{-}CO)(\mu_2,\eta^1,\eta^2\text{-}CO)\text{-}Zr(\eta^5\text{-}C_5Me_5)_2$[16] shows a Zr–O distance of 2.431 (5) Å and Zr–C of 2.272 (8) Å; hence the μ_2,η^1,η^1 designation for the bridging carbonyl of $Cp(CO)Co{=}C(CH_3)OScCp_2$.

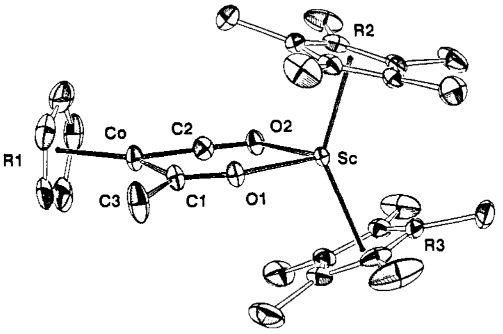


Figure 1. An ORTEP drawing of $Cp^*_2ScOC(CH_3)Co(CO)Cp$. Thermal ellipsoids are drawn at the 20% probability level.

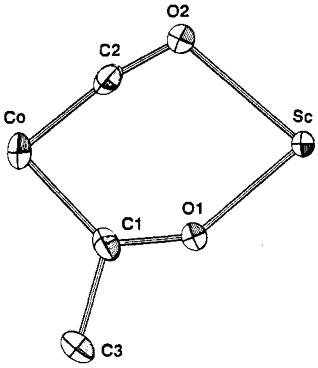
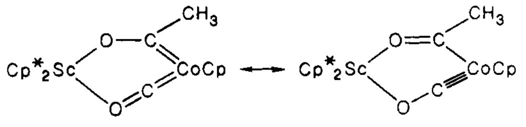
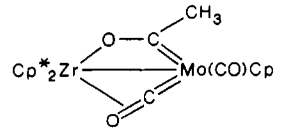


Figure 2. Skeletal view of $Cp^*_2ScOC(CH_3)Co(CO)Cp$ with Cp and Cp*'s omitted for clarity. Pertinent bond distances and angles are as follows: Sc–Co, 4.118 (1) Å; Co–C1, 1.850 (4) Å; Co–C2, 1.654 (3) Å; C1–O1, 1.268 (4) Å; C2–O2, 1.202 (4) Å; Co–C2–O2, 169.9 (3)°.

The compound most closely analogous to $CpCo(\mu_2,\eta^1,\eta^1\text{-}CO)\{{=}C(CH_3)OScCp^*_2\}$ (structures A and B) is $Cp(CO)Mo(\mu_2,\eta^1,\eta^2\text{-}CO)\{{=}C(CH_3)OZrCp^*_2\}$ (structure C).[17]



A B



C

The bonding shown in C gives rise to 18-electron, closed-

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(15) (a) Burger, B. J. Ph.D. dissertation, California Institute of Technology, Pasadena, CA, 1987. (b) Preparation of $Cp^*_2ScCH_2CH_2C_6H_5$: $Cp^*_2ScCH_3$ (0.660 g) was placed in a thick walled glass vessel. Petroleum ether (15 mL) was condensed onto the solid, and the resulting solution was cooled to −196 °C. Hydrogen (1 atm) was admitted to the vessel. The solution was then stirred at room temperature for 20 min. Volatiles were removed from the bomb at −78 °C. With the reaction vessel still at −78 °C, degassed styrene was added via syringe against an argon flush. Yellow precipitate immediately formed, which dissolved upon warming to room temperature. The solution was transferred to frit assembly in a glove box. Concentration of the solution and cooling to −78 °C afforded light yellow crystals of $Cp^*_2ScCH_2CH_2C_6H_5$, which were isolated by cold filtration (0.470 g, 56%). ^1H NMR (δ, benzene-d_6): s, 1.84 (30 H); m (AA′BB′) 1.01 (2 H), m (AA′BB′) 2.38 (2 H); d 7.30 (2 H); d 7.48 (2 H); t 7.12 (1 H). Anal. Calcd for $C_{28}H_{39}Sc$: C, 79.96; H, 9.35. Found, C, 78.75; H 9.24. Burger, B. J.; Ph.D Dissertation, California Institute of Technology, Pasadena, CA, 1987.

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Table II. Co=C and C—O Bond Lengths for Carbene Complexes of Cobalt

	d(Co=C) (Å)	*d*(C—O) (Å)	ref
$\{Ge(C_6H_5)_3\}(CO)_3Co{=}C(OCH_2CH_3)(CH_2CH_3)$	1.913 (11)	1.289 (10)	32
$Cp(CO)Co{=}CCH_2(\eta^3\text{-}CHCHCH_2)—O—ZrCp_2$	1.815 (4)	1.287 (4)	5b
$(\eta^5\text{-}C_5H_4Cl)(CO)Co{=}CCH_2(\eta^3\text{-}CHCHCH_2)—O—ZrCp_2$	1.829 (5)	1.286 (6)	5c
$Cp(C_6H_5S)Co—CN(CH_3)CH_2CH_2N(CH_3)$	1.902 (3)		4a
$(PPh_3)(CO)(NO)Co—CN(CH_3)CH_2CH(CH_3)N(CH_3)$	1.974 (15)		33
$CpCo(\mu_2,\eta^1,\eta^1\text{-}CO)\{{=}C(CH_3)OScCp^*_2\}$	1.850 (4)	1.268 (4)	this work

Table III. ^1H and ^{13}C NMR Data[a]

compound	assignmt	shift (ppm)[b]
$Cp_2MoC(CH_3)OScCp^*_2$[c,d,f]	$C_5(C\underline{H}_3)_5$	1.89
	$C_5\underline{H}_5$	4.62, 4.45
	$Mo{=}C(C\underline{H}_3)$	2.08
	$C_5(\underline{C}H_3)_5$	11.4
	$\underline{C}_5(CH_3)_5$	125.4
	$\underline{C}_5H_5$	81.7, 79.5
	$Mo{=}\underline{C}(CH_3)$	292.4
	$Mo{=}C(\underline{C}H_3)$	48.1
$Cp_2WC(H)OScCp^*_2$[d,e,f]	$C_5(C\underline{H}_3)_5$	1.93
	$C_5\underline{H}_5$	4.61, 4.53
	$W{=}C(\underline{H})$	11.07
	$\underline{C}_5(CH_3)_5$	120.3
	$C_5(\underline{C}H_3)_5$	11.2
	$\underline{C}_5H_5$	78.9, 75.6
	$W{=}\underline{C}(H)$	249.0 (J_{CH} = 124.5 Hz)
$Cp_2WC(CH_3)OScCp^*_2$[e]	$C_5(C\underline{H}_3)_5$	1.92
	$C_5\underline{H}_5$	4.49, 4.43
	$W{=}C(C\underline{H}_3)$	1.31
	$C_5(\underline{C}H_3)_5$	11.5
	$\underline{C}_5(CH_3)_5$	121.2
	$\underline{C}_5H_5$	78.4, 75.8
	$W{=}\underline{C}(CH_3)$	263.5
	$W{=}C(\underline{C}H_3)$	49.8
$Cp_2WCOSc(Cl)Cp^*_2$[e,f]	$C_5(C\underline{H}_3)_5$	1.94
	$C_5\underline{H}_5$	4.20
	$\underline{C}_5(CH_3)_5$	121.4
	$C_5(\underline{C}H_3)_5$	11.9
	$\underline{C}_5H_5$	71.6
	$W—\underline{C}O$	245.9
$Cp(CO)CoC(H)OScCp^*_2$[e,g]	$C_5(C\underline{H}_3)_5$	1.95
	$C_5\underline{H}_5$	4.92
	$Co{=}C(\underline{H})$	14.31
	$C_5(\underline{C}H_3)_5$	11.5
	$\underline{C}_5(CH_3)_5$	120.5
	$\underline{C}_5H_5$	86.2
	$Co{=}\underline{C}(H)$	284.0 (J_{CH} = 150.1 Hz)
$Cp(CO)CoC(CH_3)OScCp^*_2$[e,g]	$C_5(C\underline{H}_3)_5$	1.92
	$C_5\underline{H}_5$	4.91
	$Co{=}C(C\underline{H}_3)$	2.57
	$C_5(\underline{C}H_3)_5$	11.5
	$\underline{C}_5(CH_3)_5$	120.3
	$\underline{C}_5H_5$	85.6
	$Co{=}\underline{C}(CH_3)$	295.0
	$Co{=}C(\underline{C}H_3)$	52.6
$Cp(CO)CoC(N(CH_3)_2)OScCp^*_2$[d,e,g]	$C_5(C\underline{H}_3)_5$	1.95
	$C_5\underline{H}_5$	4.86
	$N(C\underline{H}_3)_2$	2.94, 2.61
	$C_5(\underline{C}H_3)_5$	11.6
	$\underline{C}_5(CH_3)_5$	119.6
	$\underline{C}_5H_5$	83.8
	$Co{=}C(N(\underline{C}H_3)_2)$	43.0, 35.7
	$Co{=}\underline{C}(N(CH_3)_2)$	228.8
$Cp(CO)CoC(CH_2CH_2C_6H_5)OScCp^*_2$[d,e,g]	$C_5(C\underline{H}_3)_5$	1.95
	$C_5\underline{H}_5$	4.92
	$C\underline{H}_2C\underline{H}_2C_6H_5$	3.34, 3.30
	$CH_2CH_2C_6\underline{H}_5$	7.22, 7.23
	$C_5(\underline{C}H_3)_5$	11.6
	$\underline{C}_5(CH_3)_5$	120.4
	$\underline{C}_5H_5$	85.7
	$Co{=}C(\underline{C}H_2\underline{C}H_2C_6H_5)$	68.1, 33.5
	$Co{=}C(CH_2CH_2\underline{C}_6H_5)$	142.5, 128.9, 128.6, 126.2
	$Co{=}\underline{C}(CH_2CH_2C_6H_5)$	297.6
$Cp(CO)RhC(CH_3)OScCp^*_2$[e,f]	$C_5(C\underline{H}_3)_5$	1.90
	$C_5\underline{H}_5$	5.43
	$Rh{=}C(C\underline{H}_3)$	2.56
	$C_5(\underline{C}H_3)_5$	11.5
	$\underline{C}_5(CH_3)_5$	120.5
	$\underline{C}_5H_5$	89.5
	$Rh—\underline{C}O$	206.7 ($J_{Rh\text{-}C}$ = 113.9 Hz)
	$Rh{=}\underline{C}(CH_3)$	279.1 ($J_{Rh\text{-}C}$ = 56.3 Hz)
	$Rh{=}C(\underline{C}H_3)$	53.5

[a] Unless otherwise specified, spectra were obtained in benzene-d_6 at ambient temperature, 90 MHz. [b] Chemical shifts are referenced to internal $Si(CH_3)_4$ or to solvent signals and indirectly referenced to $Si(CH_3)_4$. [c] ^1H spectrum measured at 500 MHz. [d] ^1H spectrum measured at 400 MHz. [e] ^{13}C spectrum measured at 100.38 MHz. [f] These compounds were prepared by mixing equimolar amounts of the appropriate scandium compound and metal carbonyl in benzene-d_6 in an NMR tube. The products were characterized spectroscopically and were not isolated. IR (cm^{-1}, C_6D_6, CaF_2 cells): $Cp_2W{=}C(H)OScCp^*_2$, 2723 (w), 2220 (w), 1905 (s, Cp_2WCO starting material), 1863 (m), 1566 (s), 1429 (m), 1387 (m), 1200 (s); $Cp_2W{=}COScCp^*_2$, 1905 (s, Cp_2WCO starting material), 1835 (s), 1424 (br), 1378 (w), 1340 (w); $Cp_2Mo{=}C(CH_3)OScCp^*_2$, 1948 (s, Cp_2MoCO starting material), 1175 (s), 1104 (s), 1060 (m), 1035 (m); $Cp(CO)Rh{=}C(CH_3)OScCp^*_2$, 2041 (s, $CpRh(CO)_2$ starting material), 1978 (s), 1805 (s), 1765 (w), 1420 (br). [g] Signals for the CO were not observed, presumably due to ^{59}Co quadroplar broadening.

shell valence shells for both molybdenum and zirconium. Thus, there are two major differences between these two structures: (a) a metal–metal bond for C, as indicated by the relatively short Zr–Mo bond distance (3.297 (1) Å; cf. the 4.118 (1) Å Sc–Co distance), and (b) the bridging carbonyl is of the μ_2,η^1,η^2-type (ν(CO) = 1536 cm^{-1}, *d*(C–O) = 1.241 (4) Å) for $Cp(CO)Mo(\mu_2,\eta^1,\eta^2\text{-}CO)\{{=}C(CH_3)OZrCp^*_2\}$, compared with the μ_2,η^1,η^1-carbonyl for $CpCo(\mu_2,\eta^1,\eta^1\text{-}CO)\{{=}C(CH_3)OScCp^*_2\}$ (ν(CO) = 1795 cm^{-1}, *d*(C–O) = 1.202 (4) Å). Caution[17b] has earlier noted that the acetyl/oxycarbene ligand is quite flexible, spanning metal–metal distances from 2.57–3.52 Å. The nonbonding Sc–Co distance of 4.118 (1) Å indicates that even greater metal–metal distances may be accommodated. Other examples of complexes having a μ_2,η^1,η^1-CO ligand are given in Table I. Norton has noted that carbonyl stretching frequencies for μ_2,η^1,η^1 and μ_2,η^1,η^2 types are so similar that the position may not be used as diagnostic.[17a] Interestingly, the ν(CO) for the μ_2,η^1,η^1-CO of $CpCo(\mu_2,\eta^1,\eta^1\text{-}CO)\{{=}C(CH_3)OScCp^*_2\}$ (1795 cm^{-1}) is substantially greater than the 1530–1630 cm^{-1} region observed for other members of these two series. The modest distortion from a linear Co–C–O arrangement (169.9 (3)°) in the six-membered ring likely reduces back-bonding from the cobalt.

The structural features of the $[Cp^*_2Sc]$ unit are unexceptional in comparison to other structurally characterized $[Cp^*_2Sc]$ compounds.[9,18] The Sc–O distances compare

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[18] Thompson, M. E.; Bercaw, J. E. *Pure Appl. Chem.* **1984**, *56*, 1–11.

with those for the carboxylate derivative $Cp^*_2ScO_2CC_6H_4CH_3$ (d(Sc–O) = 2.167 (3) and 2.176 (3) Å).[19]

The carbon–oxygen bond for the bridging methylscandoxycarbene ligand (1.268 (4) Å) is significantly longer than that for the μ_2,η^1,η^1-CO ligand, indicating a substantially lower C–O bond order. The cobalt–carbon bond length (1.654 (3) Å) for the μ_2,η^1,η^1 carbonyl is roughly the same as for $CpCo(CO)_2$ (1.679 (4) Å),[20] and the cobalt–carbene carbon distance is ca. 0.2 Å longer (1.850 (4) Å). This modest lengthening of the metal–carbon bond on conversion to an oxycarbene is normal, although multiple metal–carbon bonding is maintained (cf. a typical Co–C single bond length ≈2.0 Å).[21] Several other cobalt carbene compounds have been structurally characterized, and some structural parameters are summarized in Table II.

The bond distances and angles are most indicative of resonance structure A, although the small difference in d(C1–O1) and d(C2–O2) could be taken as signifying some B character. The chelating oxygen ligation about the scandium center for $CpCo(\mu_2,\eta^1,\eta^1\text{-CO})\{{=}C(CH_3)OScCp^*_2\}$ leads to a lower reactivity. For example, in contrast to $Cp_2W{=}C(CH_3)O\text{-}ScCp^*_2$, $CpCo(\mu_2,\eta^1,\eta^1\text{-CO})\{{=}C(CH_3)OScCp^*_2\}$ does not react with H_2 after days at 80 °C.

Conclusion

The increased Lewis acidity of the 14-electron Sc center results in greater reactivity toward activation of metal carbonyls, relative to other early-transition-metal or aluminum compounds. The resulting polarization of the carbonyl C–O bond results in a greater susceptibility to nucleophilic attack (at carbon) by the migrating R group. When $L_nM\text{-}CO$ is Cp_2MCO (M = Mo, W), the type of R that may be added is limited by steric interactions with the Cp rings. When $L_nM\text{-}CO$ is $CpM(CO)_2$ (M = Co, Rh), bulkier alkyls and amides may be added. The structure of $CpCo(\mu_2,\eta^1,\eta^1\text{-CO})\{{=}C(CH_3)OScCp^*_2\}$ illustrates, once again, the oxophilic nature of the Sc center as it coordinates both carbonyl oxygens.

Experimental Section

General Considerations. All manipulations of air- and/or water-sensitive materials were carried out by using high vacuum techniques or in a drybox under an atmosphere of dinitrogen as described elsewhere.[22] Solvents were dried and purified by prolonged reflux over a suitable drying agent followed by distillation under an atmosphere of dinitrogen. Ethereal solvents were stored over sodium benzophenone ketyl, and hydrocarbon solvents were stored over titanocene.[23] Elemental analyses were provided by the Caltech microanalytical service. Nuclear magnetic resonance spectra were recorded on a Varian EM 390, JEOL FX90Q, Bruker WM 500, or JEOL GX400Q spectrometer. Infrared spectra were recorded on a Beckman 4240 spectrometer and are reported from 2800 to 1000 cm^{-1}. Relative intensities are abbreviated as follows: vs (very strong), s (strong), m (medium) w (weak), bd (broad), sh (shoulder). $Cp^*_2ScCH_3$,[9] $Cp^*_2ScCD_3$,[9] $Cp^*_2ScH(THF)$,[9] $Cp^*_2ScC_6H_5$,[9] $Cp^*_2ScC{\equiv}CCH_3$,[9] $Cp^*_2ScN(CH_3)_2$,[11] $Cp^*_2ScCH_2CH_2C_6H_5$,[15b] $Cp^*_2ScCH(Si(CH_3)_3)_2$,[24] Cp_2MoCO,[25] and Cp_2WCO[26] and were prepared according to previously reported procedures. $CpCo(CO)_2$ was obtained from Alfa, and $CpRh(CO)_2$ was obtained from Strem; both were used as received. $CpRh(^{13}CO)_2$ and $Cp_2W(^{13}CO)$ were prepared by photolysis of $CpRh(CO)_2$ and Cp_2WCO, respectively, under 1 atm of ^{13}CO (Monsanto-Mound facility).

$Cp_2W{=}C(CH_3)\{OScCp^*_2\}$. $Cp^*_2ScCH_3$ (0.173 g, 0.51 mmol) and 0.175 g of Cp_2WCO (0.52 mmol) were dissolved in toluene (10 mL) and allowed to stir overnight. The color of the solution changes gradually from green to brown as the reaction progresses. The solvent was removed under reduced pressure, and n-pentane (3 mL) was distilled in. The flask and frit were cooled to −78 °C and filtered, yielding 0.205 g of brown powder, $Cp^*_2ScOC(CH_3)WCp_2$ (60%). IR (cm^{-1}, Nujol) 2725 (w), 1900 (br), 1455 (s), 1379 (s), 1167 (s), 1063 (m), 1017 (m). Cp_2WH_2 impurity in Cp_2WCO prevented accurate elemental analysis.

$Cp(CO)Co{=}C(H)\{OScCp^*_2\}$. $Cp^*_2ScH(THF)$ (0.195 g, 0.51 mmol) was dissolved in toluene (10 mL), and 64 μL of $CpCO(CO)_2$ (0.095 g, 0.53 mmol) was added to the solution. The orange solution was allowed to stir at room temperature overnight. Volatiles were removed under reduced pressure, and n-pentane (2 mL) was vacuum transferred onto the residue. The flask and frit were cooled to −78 °C and filtered. Yellow-orange, microcrystalline $Cp^*_2ScOCHCo(CO)Cp$ (0.160 g, 55%) was obtained. Anal. Calcd for $C_{27}H_{36}O_2ScCo$: C, 65.32; H, 7.31. Found: C, 64.97; H, 7.15. IR (cm^{-1}, Nujol): 2590 (w), 1840 (s), 1798 (sh), 1342 (sh), 1108 (w), 1050 (w), 1005 (w).

$Cp(CO)Co{=}C(CH_3)\{OScCp^*_2\}$. The procedure is the same as that for $Cp^*_2ScOCHCo(CO)Cp$ except that 0.503 g (1.52 mmol) of $Cp^*_2ScCH_3$ and 187 μL of $CpCo(CO)_2$ (0.274 g, 1.52 mmol) yield 0.545 g (70%) of dark orange, microcrystalline $Cp^*_2ScOC(CH_3)Co(CO)Cp$. Anal. Calcd for $C_{28}H_{38}O_2ScCo$: C, 65.88; H, 7.50. Found: C, 65.64; H, 7.44. IR (cm^{-1}, Nujol): 2720 (w), 2015 (w), 1962 (w), 1795 (s), 1616 (w), 1082 (m), 1018 (m).

$Cp(CO)Co{=}C(CH_2CH_2C_6H_5)\{OScCp^*_2\}$. The procedure is the same as that for $Cp(CO)Co{=}C(H)\{OScCp^*_2\}$ except that 0.208 g of $Cp^*_2ScCH_2CH_2C_6H_5$ (0.50 mmols) and 60 μL of $CpCo(CO)_2$ (0.089 g, 0.49 mmol) yield 0.153 g (52%) of the red-orange $Cp(CO)Co{=}C(CH_2CH_2C_6H_5)\{OScCp^*_2\}$. Anal. Calcd for $C_{35}H_{44}O_2ScCo$: C, 69.99; H, 7.38. Found: C, 70.22; H, 7.62. IR (cm^{-1}, Nujol): 2718 (w), 1805 (s), 1757 (sh), 1600 (w), 1492 (w), 1410 (m), 1322 (s), 1309 (m), 1230 (w), 1110 (w), 1040 (w), 1010 (w).

$Cp(CO)Co{=}C(NMe_2)\{OScCp^*_2\}$. The procedure is the same as that for $Cp^*_2ScOCHCo(CO)Cp$ except that 0.150 g of $Cp^*_2ScN(CH_3)_2$ (0.42 mmol) and 51 μL (0.076 g, 0.42 mmols) of $CpCo(CO)_2$ yield 0.132 g of $Cp^*_2ScOC(N(CH_3)_2)$. Anal. Calcd for $C_{29}H_{41}NO_2ScCo$: C, 64.56; H, 7.65; N, 2.60. Found: C, 65.47; H, 7.75; N, 2.20. IR (cm^{-1}, Nujol): 2722 (w), 2028 (w), 1795 (s), 1742 (w), 1495 (m), 1434 (m), 1399 (w), 1380 (m), 1300 (s), 1240 (m), 1085 (s), 1050 (w), 1018 (w).

Crystal Structure Determination of $CpCo(\mu_2,\eta^1,\eta^1\text{-CO})$-

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[24] Preparation of $Cp^*_2ScCH(Si(CH_3)_3)_2$: 0.250 g of Cp^*_2ScCl and 0.120 g of $LiCH(Si(CH_3)_3)_2$ were mixed in 30 mL of toluene and allowed to stir overnight. Toluene was removed in vacuo and 8 mL of n-pentane vacuum transferred onto the reaction mixture. LiCl was filtered off, and the filtrate was cooled to −78 °C. The resulting yellow microcrystals were collected by cold filtration (0.202 g, 60%). ^{1}H NMR (δ, benzene-d_6): s 1.92 (15 H); s 1.85 (15 H); s 1.32 (1 H); s 0.25 (18 H). Anal. Calcd for $C_{27}H_{49}Si_2Sc$: C, 66.93; H, 9.60. Found: C, 67.04; H, 9.45. Bunel, E. B. Ph.D. Dissertation, California Institute of Technology, Pasadena, CA, 1988.

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Table IV. Atom Coordinates and U_{ij}'s ($\times 10^4$)

atom	x	y	z	U_{eq}, Å^2
Co	607.5 (6)	−554.2 (4)	−2335.5 (4)	584 (1)
Sc	3749.4 (6)	2711.1 (5)	−2583.8 (4)	339 (1)
C1	2705 (4)	−240 (3)	−2534 (3)	560 (9)
O1	3621 (2)	803 (2)	−2573 (2)	481 (5)
C2	727 (4)	970 (3)	−2397 (3)	534 (9)
O2	1062 (3)	2082 (2)	−2444 (2)	543 (6)
C3	3585 (6)	−1320 (4)	−2663 (4)	961 (16)
C11	−223 (8)	−2480 (4)	−2650 (5)	1007 (18)
C12	−1518 (7)	−1889 (5)	−2849 (5)	1062 (18)
C13	−1605 (6)	−1307 (5)	−1965 (6)	1047 (18)
C14	−388 (8)	−1594 (6)	−1310 (4)	1058 (18)
C15	463 (7)	−2278 (5)	−1710 (5)	1054 (18)
C21	6173 (4)	3901 (3)	−1479 (2)	515 (8)
C22	4883 (4)	4498 (3)	−1404 (2)	526 (9)
C23	3746 (4)	3647 (4)	−1023 (2)	562 (9)
C24	4362 (4)	2549 (3)	−862 (2)	539 (9)
C25	5848 (4)	2721 (3)	−1159 (2)	545 (9)
C21M	7806 (5)	4505 (5)	−1679 (3)	893 (14)
C22M	4805 (7)	5855 (4)	−1516 (3)	988 (16)
C23M	2253 (6)	3972 (5)	−760 (3)	1043 (16)
C24M	3623 ′7)	1450 (4)	−380 (3)	1005 (16)
C25M	6953 (6)	1777 (5)	−1076 (4)	1038 (15)
C31	2179 (4)	2681 (3)	−4227 (2)	553 (9)
C32	3457 (5)	2106 (3)	−4282 (2)	596 (9)
C33	4894 (4)	2985 (5)	−4014 (3)	702 (12)
C34	4460 (5)	4147 (4)	−3807 (2)	693 (12)
C35	2768 (5)	3929 (3)	−3920 (2)	558 (9)
C31M	416 (5)	2054 (5)	−4533 (3)	1044 (17)
C32M	3360 (8)	788 (5)	−4637 (3)	1191 (18)
C33M	6561 (6)	2787 (8)	−4057 (4)	1551 (25)
C34M	5570 (9)	5397 (5)	−3710 (3)	1503 (24)
C35M	1734 (8)	4879 (5)	−3812 (3)	1177 (18)

Table V. Bond Lengths (Å) and Angles (deg)

Bond Lengths

Sc–C21	2.506 (3)	C11–C12	1.376 (9)
Sc–C22	2.505 (3)	C11–C15	1.388 (9)
Sc–C23	2.486 (4)	C22–C22M	1.507 (6)
Sc–C24	2.493 (3)	C12–C13	1.452 (9)
Sc–C25	2.485 (3)	C22–C23	1.419 (5)
Sc–C31	2.525 (4)	C13–C14	1.367 (9)
Sc–C32	2.517 (4)	C23–C24	1.406 (5)
Sc–C33	2.478 (4)	C14–C15	1.337 (9)
Sc–C34	2.492 (4)	C23–C23M	1.507 (6)
Sc–C35	2.493 (4)	C21–C22	1.407 (5)
Sc–O1	2.067 (2)	C24–C25	1.406 (5)
Sc–O2	2.331 (2)	C21–C25	1.377 (5)
Sc–R2	2.192	C24–C24M	1.502 (6)
Sc–R3	2.199	C21–C21M	1.518 (6)
C1–O1	1.268 (4)	C31–C32	1.377 (5)
C1–C3	1.542 (6)	C25–C25M	1.519 (6)
C2–O2	1.202 (4)	C31–C35	1.397 (5)
Co–C11	2.105 (6)	C31–C31M	1.519 (6)
Co–C12	2.117 (6)	C32–C33	1.400 (6)
Co–C13	2.099 (6)	C32–C32M	1.505 (7)
Co–C14	2.112 (6)	C33–C34	1.431 (6)
Co–C15	2.103 (6)	C33–C33M	1.500 (8)
Co–C1	1.850 (4)	C34–C35	1.405 (5)
Co–C2	1.654 (3)	C34–C34M	1.500 (7)
Co–R1	1.748	C35–C35M	1.510 (7)

Bond Angles

O1–Sc–O2	80.49 (8)	C25–C24–C23	107.4 (3)
Sc–O1–C1	144.8 (2)	C24M–C24–C23	125.5 (3)
Sc–O2–C2	110.9 (2)	C24M–C24–C25	126.9 (3)
C3–C1–O1	110.7 (3)	C24–C25–C21	109.1 (3)
C1–Co–C2	85.1 (2)	C25M–C25–C21	126.0 (3)
Co–C1–C3	120.9 (3)	C25M–C25–C24	124.7 (3)
Co–C1–O1	128.5 (3)	C35–C31–C32	109.3 (3)
Co–C2–O2	169.9 (3)	C31M–C31–C32	124.1 (3)
C15–C11–C12	109.5 (6)	C31M–C31–C35	126.5 (3)
C13–C12–C11	104.8 (5)	C33–C32–C31	108.6 (3)
C14–C13–C12	107.3 (5)	C32M–C32–C31	126.7 (4)
C15–C14–C13	109.8 (6)	C32M–C32–C33	124.6 (4)
C14–C15–C11	108.5 (6)	C34–C33–C32	107.2 (3)
C25–C21–C22	108.4 (3)	C33M–C33–C32	126.2 (4)
C21M–C21–C22	126.8 (3)	C33M–C33–C34	126.1 (4)
C21M–C21–C25	123.7 (3)	C35–C34–C33	107.2 (3)
C23–C22–C21	107.4 (3)	C34M–C34–C33	125.1 (4)
C22M–C22–C21	128.0 (3)	C34M–C34–C35	126.3 (4)
C22M–C22–C23	123.7 (3)	C34–C35–C31	107.7 (3)
C24–C23–C22	107.7 (3)	C35M–C35–C31	125.0 (4)
C23M–C23–C22	123.8 (3)	C35M–C35–C34	127.1 (4)
C23M–C23–C24	128.2 (3)		

$\{=C(CH_3)OScCp^*{}_2\}$. A single crystal (dimensions 0.21 × 0.43 × 0.76 mm), grown by slow cooling of a saturated solution of toluene, was placed in a glass capillary and sealed under nitrogen. The capillary was mounted on a CAD4 diffractometer equipped with graphite monochromator and Mo Kα radiation. The preliminary photographic workup indicated a symmetry no higher than $\bar{1}$; we assigned space group $P\bar{1}$ with $Z = 2$. The least-squares refinement of the orientation matrix with the setting angles of 25 reflections generated the following cell parameters: $a = 8.592$ (4) Å, $b = 10.923$ (2) Å, $c = 14.648$ (2) Å, $\alpha = 91.074$ (14)°, $\beta = 100.84$ (2)°, $\gamma = 100.77$ (3)°, $V = 1324.35$ (66) Å^3. Intensity data were collected by θ–2θ scans of width 2.00° (plus disperson) at 6°/min for the Ewald sphere $(\pm h, \pm k, \pm l)$ to $2\theta = 50°$ (13156 reflections). The three check reflections indicated no decomposition. The data were averaged over 1 symmetry (average goodness of fit = 1.19, 3378 reflections; and $R = 0.036$ for the 2930 paired reflections), 1185 reflections were deleted, and the remaining data were reduced to F_o^2. The form factors were taken from ref 34; those for the Co and the Sc were corrected for f' and f''.

The coordinates of the scandium and cobalt atoms were derived from the Patterson map, and the remainder of the structure was derived from subsequent F_o and ΔF Fourier maps. The hydrogen atoms were placed at idealized positions with $B = 9.0$ Å^3 and were not refined. The full-matrix least-squares refinement of atom coordinates and U_{ij}'s of non-hydrogen atoms, the scale factor, and a term of isotropic secondary extinction (g 1.6 (2) × 10^{-6}) minimizing $\sum w[F_o)^2 - (F_c/k)^2]^2$ yielded a goodness of fit $= \{\sum w[(F_o)^2 - (F_c/k)^2]^2/(n - p)\}^{1/2} = 3.51$ ($n = 4593$ reflections, $p = 290$ parameters), $R_F = \sum||F_o| - F_c||/\sum|F_o| = 0.055$ (4391 reflections, $I > 0$), and $R'_F = 0.046$ (3724 reflections, $I > 3\sigma$); the largest peak in the $\Delta\rho$ map was approximately 0.5 e/Å^3. The atom coordinates and U_{eq}'s for non-hydrogen atoms are given in Table IV, and bond lengths and angles are given in Table V. Table 1 (supplementary material) (U_{ij}'s for non-hydrogen atoms), Table 2 (supplementary material) (atom coordinates for hydrogen atoms), Table 3 (supplementary material) (least-squares planes), and Table 4 (supplementary material) (a listing of structure factor amplitudes: I, $10F_o$, $10F_c$, $10[(F_o^2 - F_c^2)/\sigma_{F2}]$) have been deposited.

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Registry No. $Cp^*{}_2ScCH_3$, 99707-15-0; $Cp^*{}_2ScH(THF)$, 105563-98-2; $Cp^*{}_2ScN(CH_3)_2$, 99707-10-5; $Cp^*{}_2ScCH_2CH_2C_6H_5$, 117024-43-8; $Cp^*{}_2ScCH(Si(CH_3)_3)_2$, 117024-46-1; Cp_2WCO, 39333-44-3; $CpCo(CO)_2$, 12078-25-0; $Cp_2W{=}C(CH_3)OScCp^*{}_2$, 117024-42-7; $Cp(CO)Co{=}C(H)\{OScCp^*{}_2\}$, 117041-22-2; $Cp(CO)Co{=}C(CH_3)\{OScCp^*{}_2\}$, 117041-23-3; $Cp(CO)Co{=}C(CH_2CH_2C_6H_5)\{OScCp^*{}_2\}$, 117041-24-4; $Cp(CO)Co{=}C(NMe_2)\{OScCp^*{}_2\}$, 117041-25-5; $Cp^*{}_2ScCl$, 105563-94-8; $LiCH(Si(CH_3)_3)_2$, 41823-71-6; $Cp_2MoC(CH_3)OScCp^*{}_2$, 117024-44-9; $Cp_2WC(H)OScCp^*{}_2$, 117024-45-0; $Cp_2WCOSc(Cl)Cp^*{}_2$, 117041-26-6; $Cp(CO)RhC(CH_3)OScCp^*{}_2$, 100-42-5.

Supplementary Material Available: Table 1 (U_{ij}'s for non-hydrogen atoms), Table 2 (atom coordinates for hydrogen atoms), and Table 3 (least-squares planes) (3 pages); Table 4 (a listing of structure factor amplitudes: I, $10F_o$, $10F_c$, $10[(F_o^2 - F_c^2)/\sigma_{F^2}]$) (18 pages). Ordering information is given on any current masthead page.

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(34) *International Tables of X-Ray Crystallography*; Kynoch: Birmingham, England, 1900; Vol. IV, Table 2.2B, pp 99–101.