

Table IV. Crystal Data

formula	$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^6\text{-C}_6\text{H}_6)]\text{PF}_6\cdot 2\alpha\text{-CD}\cdot 8\text{H}_2\text{O}$
cryst syst	triclinic
space group	$P1$
a , Å	13.815 (1)
b , Å	13.929 (1)
c , Å	15.639 (2)
α , deg	94.23 (1)
β , deg	87.15 (1)
γ , deg	119.81 (1)
V , Å ³	2604
Z	1
calc density, g/cm ³	1.552
no. of reflns	10226
no. of obs reflns	9965
no. of parameters	1432
final R factor	0.083

cesively with water and ethanol, giving 1.0 g (87%) of $[\text{cpFe}(\eta^6\text{-C}_6\text{H}_6)]\text{PF}_6\cdot 2\alpha\text{-CD}\cdot 8\text{H}_2\text{O}$ as orange-yellow crystals, mp 260 °C (dec). Anal. Calcd for $\text{C}_{83}\text{H}_{131}\text{F}_6\text{FeO}_{60}\text{P}\cdot 8\text{H}_2\text{O}$: C, 40.96; H, 6.09; F, 4.68; Fe, 2.29; P, 1.27. Found: C, 41.23; H, 6.09; F, 4.70; Fe, 2.31; P, 1.24.

The α -CD adduct of the analogous BF_4^- salt was prepared and isolated in essentially the same manner in 26% yield. Anal. Calcd for $\text{C}_{83}\text{H}_{131}\text{BF}_4\text{FeO}_{60}\cdot 8\text{H}_2\text{O}$: C, 41.96; H, 6.24; F, 3.20. Found: C, 41.80; H, 6.35; F, 3.21.

The β -CD adduct of the PF_6^- salt was prepared in a similar way, using hot saturated β -CD solutions, yield 44%. Anal. Calcd for $\text{C}_{95}\text{H}_{151}\text{F}_6\text{FeO}_{70}\text{P}\cdot 7\text{H}_2\text{O}$: C, 41.64; H, 6.07; F, 4.16; Fe, 2.04; P, 1.13. Found: C, 41.38; H, 6.11; F, 4.25; Fe, 2.07; P, 1.16.

Crystal Structure Analysis. Crystals of $[\text{cpFe}(\eta^6\text{-C}_6\text{H}_6)]\text{PF}_6\cdot 2\alpha\text{-CD}\cdot 8\text{H}_2\text{O}$ were obtained as yellow, transparent prisms from aqueous solution. The sample crystal was sealed with epoxy to the end of a glass fiber. Crystal data are summarized in Table IV. A Nonius CAD4 automatic diffractometer was used for data collection with Cu K α radiation and graphite monochromator. At room temperature the intensities of 10 226 independent re-

flections with $\theta < 70^\circ$ were measured, of which 9965 were classified as observed with $I > 2\sigma(I)$. The crystal showed no significant intensity decay during data collection. The structure was solved with data from an isomorphous crystal of the complex $\text{LiI}_3\cdot \text{I}_2\cdot 2\alpha\text{-CD}\cdot 8\text{H}_2\text{O}$.²³ The coordinates of one cyclodextrin molecule were submitted to the program ORIENT of the DIRDIF program system.²⁵ In a subsequent electron density map 115 of the 132 atoms of the two cyclodextrin molecules could be localized. Successive full-matrix least-squares refinements and difference Fourier syntheses revealed the positions of all non-hydrogen atoms. Anisotropic temperature factors were introduced for all atoms. Due to the large number of parameters, further refinements were carried out in segments. The final R value was 0.083 for all 9965 data with $I > 2\sigma(I)$. Hydrogen atoms could not be localized. The positions of those of the guest molecule were calculated.

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Registry No. $[\text{cpFe}(\eta^6\text{-C}_6\text{H}_6)]\text{PF}_6\cdot 2\alpha\text{-CD}\cdot 8\text{H}_2\text{O}$, 125049-68-5; $[\text{cpFe}(\eta^6\text{-C}_6\text{H}_6)]\text{BF}_4\cdot 2\alpha\text{-CD}\cdot 8\text{H}_2\text{O}$, 125049-69-6; $[\text{cpFe}(\eta^6\text{-C}_6\text{H}_6)]\text{PF}_6\cdot 2\beta\text{-CD}\cdot 7\text{H}_2\text{O}$, 125049-70-9.

Supplementary Material Available: Listings of bond distances and angles, O...O distances suggesting hydrogen bonds, and anisotropic thermal parameters (9 pages); listings of observed and calculated structure factors (47 pages). Ordering information is given on any current masthead page.

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Reaction of $\text{Cp}_3\text{U}=\text{CHPMeRPh}$ with $\text{CpCo}(\text{CO})_2$

Roger E. Cramer,* Jong Hwa Jeong, Paul N. Richmann, and John W. Gilje*

Chemistry Department, University of Hawaii, Honolulu, Hawaii 96822

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A terminal carbonyl of $\text{CpCo}(\text{CO})_2$ inserts into the $\text{U}=\text{C}$ bond of $\text{Cp}_3\text{U}=\text{CHPMeRPh}$ ($\text{R} = \text{Ph}$ or Me) to produce $\text{Cp}(\text{OC})\text{CoC}(\text{OUCp}_3)=\text{CHPMeRPh}$. The structure of $\text{Cp}(\text{OC})\text{CoC}(\text{OUCp}_3)=\text{CHPMe}_2\text{Ph}$ has been confirmed by X-ray diffraction: space group $P2_12_12_1$; $a = 15.645$ (2) Å, $b = 23.828$ (3) Å, $c = 15.140$ (3) Å, $\alpha = \beta = \gamma = 90^\circ$; final error indexes $R = 0.0555$, $R_G = 0.0644$ for 3433 unique data with $I > 3\sigma(I)$. Heating $\text{Cp}(\text{OC})\text{CoC}(\text{OUCp}_3)=\text{CHPMeRPh}$ leads to the formation of $\text{Cp}(\text{OC})\text{CoPMeRPh}$.

We are interested in utilizing the oxygen affinity of actinides to activate small molecules.¹ In this regard we have determined that the α -carbon atom of $\text{Cp}_3\text{U}=\text{CHPMeRPh}$ ($\text{Me} = \text{CH}_3$, $\text{Ph} = \text{C}_6\text{H}_5$, $\text{Cp} = \text{C}_5\text{H}_5$) is a strong nucleophile² and that polar unsaturated molecules will insert into the uranium-carbon multiple bond³⁻⁵ of $\text{Cp}_3\text{U}=\text{CHPMeRPh}$.⁶⁻⁹ We are investigating the reactions

of $\text{Cp}_3\text{U}=\text{CHPMeRPh}$ with a variety of metal carbonyls and have previously reported the reactions of $\text{M}(\text{CO})_6$ ($\text{M} = \text{W}$, Mo , Cr),^{10,11} $\text{CpMn}(\text{CO})_3$,¹² and $[\text{CpFe}(\text{CO})_2]_2$ ¹³ with

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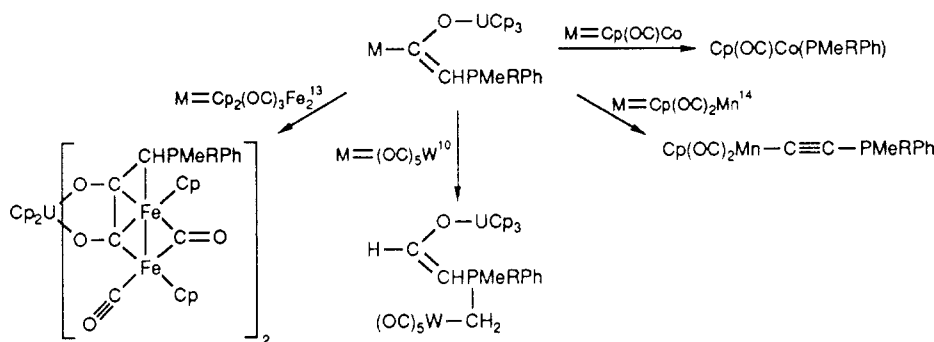
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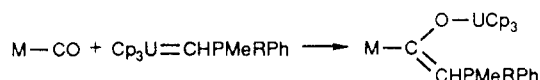
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Scheme I. Reactions of $\text{MC}(\text{OUCp}_3)=\text{CHPMeRPh}$ 

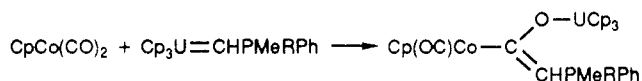
$\text{Cp}_3\text{U}=\text{CHPMeRPh}$. For all of these a terminal carbonyl inserts into the uranium-carbon multiple bond:



X-ray structures show that the uranium is tightly coordinated to oxygen and that all four electrons from the uranium-carbon bond are utilized to form a new carbon-carbon multiple bond.^{2,12} As a result the carbonyl is activated toward further reactions such as carbon-oxygen bond cleavage,¹⁴ carbonyl coupling,¹³ and an unusual isomerization reaction.¹⁰ Here we report the reaction of $\text{Cp}_3\text{U}=\text{CHPMeRPh}$ with $\text{CpCo}(\text{CO})_2$.

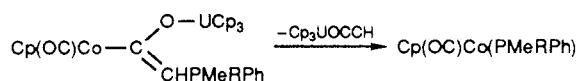
Results and Discussion

The initial reaction of $\text{CpCo}(\text{CO})_2$ with $\text{Cp}_3\text{U}=\text{CHPMeRPh}$ is the insertion of a terminal carbonyl into the $\text{U}=\text{C}$ bond:



While the NMR spectrum of $\text{Cp}(\text{OC})\text{CoC}(\text{OUCp}_3)=\text{CHPMeRPh}$, which displays large chemical shifts due to the presence of paramagnetic $\text{U}(\text{IV})$, is consistent with the X-ray structure, the chemical shift of the CH in $\text{Cp}(\text{OC})\text{CoC}(\text{OUCp}_3)=\text{CHPMeRPh}$ [15.1 (R = Me), 14.4 ppm (R = Ph)] is much less than those reported for the analogous protons in $(\text{OC})_5\text{WC}(\text{OUCp}_3)=\text{CHPMeRPh}$ [28.7 (R = Me), 26.0 ppm (R = Ph)]¹⁰ and $\text{Cp}(\text{OC})_2\text{MnC}(\text{OUCp}_3)=\text{CHPMe}_2\text{Ph}$ [32.5 ppm].¹² Since the magnitude of chemical shifts in these compounds should reflect the separation of the paramagnetic center and the nucleus whose resonance is being observed, the smaller CH shift in $\text{Cp}(\text{OC})\text{CoC}(\text{OUCp}_3)=\text{CHPMeRPh}$, as compared to $(\text{OC})_5\text{WC}(\text{OUCp}_3)=\text{CHPMeRPh}$ and $\text{Cp}(\text{OC})_2\text{MnC}(\text{OUCp}_3)=\text{CHPMe}_2\text{Ph}$, probably reflects a greater $\text{U}\cdots\text{H}-\text{C}$ distance in the cobalt complex (see below). The IR spectrum of solid $\text{Cp}(\text{OC})\text{CoC}(\text{OUCp}_3)=\text{CHPMeRPh}$ is also unexpected, showing two peaks in the C-O stretching region rather than the single absorption expected for a monocarbonyl derivative. The structure of $\text{Cp}(\text{OC})\text{CoC}(\text{OUCp}_3)\text{CHPMe}_2\text{Ph}$, which is discussed below, provides a rationalization for these features.

Upon being heated, $\text{Cp}(\text{OC})\text{CoC}(\text{OUCp}_3)\text{CHPMeRPh}$ forms $\text{Cp}(\text{OC})\text{Co}(\text{PMeRPh})$:



By NMR this reaction is quantitative, and we have obtained no evidence of an isomerization similar to that which occurs in $(\text{OC})_5\text{WC}(\text{OUCp}_3)=\text{CHPMeRPh}$ ¹⁰ or of

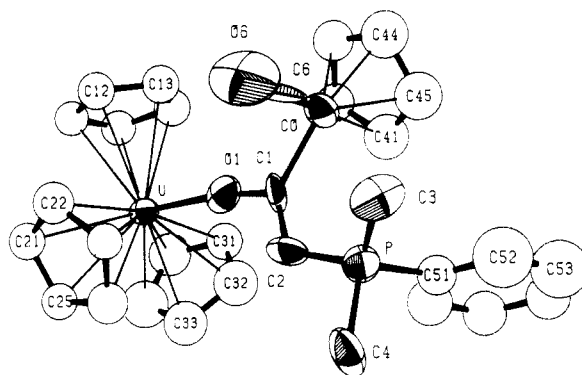


Figure 1. ORTEP drawing of $\text{Cp}(\text{OC})\text{CoC}(\text{OUCp}_3)=\text{CHPMe}_2\text{Ph}$.

acetylide formation such as in $\text{Cp}(\text{OC})_2\text{MnC}(\text{OUCp}_3)=\text{CHPMeRPh}$.¹⁴ Assuming the formula written above, the precipitate that forms during this thermolysis should have the composition Cp_3UOCCH . The crude precipitate gave an analysis close to that expected for this composition. There are no peaks between 1650 and 2500 cm^{-1} and near 940 cm^{-1} in the IR spectrum, and no organic materials arising from the " $-\text{OCCH}$ " group could be detected in the mass spectrum of the precipitate after it had been exposed to moisture or in the NMR of the precipitate after it had been exposed to water, methanol, or acetic acid. On the basis of these data, we believe that thermolysis of $\text{Cp}(\text{OC})\text{CoC}(\text{OUCp}_3)\text{CHPMeRPh}$ does not produce a simple $-\text{OCCH}$ ligand and may indeed produce a polymer. In support of this hypothesis, we were unable to find solvents in which the precipitate is soluble and were not able to obtain crystalline material for a possible X-ray analysis.

We have now reported the behavior of $\text{M}-\text{C}(\text{OUCp}_3)\text{CHPR}_3$ for M groups containing four separate metals.^{10,13,14} In all cases, these have proven to be reactive molecules that yield decomposition or rearrangement products under modest heating (see Scheme I). In all cases, the $\text{U}-\text{O}$ bond remains intact as does the $\text{C}=\text{C}$ double bond, $\text{C1}-\text{C2}$ in this case. Earlier we reported examples involving the breaking of $\text{C}-\text{O}$, $\text{C}-\text{M}$, and/or $\text{C}-\text{H}$ bonds. The present case provides another example of $\text{M}-\text{C}$ cleavage plus the first example of $\text{C}-\text{P}$ cleavage. Thus, each of these compounds has produced different products, even among such similar species as $\text{Cp}(\text{OC})_2\text{MnC}(\text{OUCp}_3)\text{CHPMe}_2\text{Ph}$ and $\text{Cp}(\text{OC})\text{CoC}(\text{OUCp}_3)\text{CHPMe}_2\text{Ph}$. We are continuing our investigations of this fascinating series of molecules.

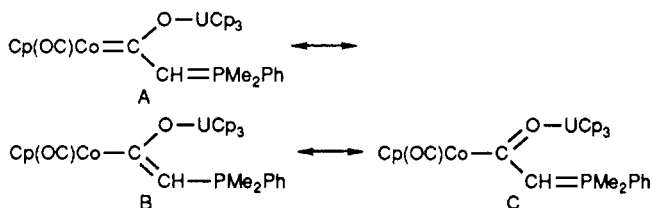
Structure of $\text{Cp}(\text{OC})\text{CoC}(\text{OUCp}_3)\text{CHPMe}_2\text{Ph}$. The asymmetric unit contains two independent molecules of $\text{Cp}(\text{OC})\text{CoC}(\text{OUCp}_3)\text{CHPMe}_2\text{Ph}$ that differ only by rotation about the $\text{C1}-\text{Co}$ and $\text{C2}-\text{P}$ bonds. An ORTEP drawing

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of one of these is shown in Figure 1. Bond distances and angles, which are summarized in Tables IV and V, are identical within experimental uncertainty for the two molecules; unless the two molecules are being compared, averaged values are quoted in the subsequent discussion. However, due to differences in crystal packing there are significant differences in some intermolecular contacts (see below).

The geometry about uranium is approximately tetrahedral. Both the bond angles and U-Cp distances are in the range observed in other Cp_3UX complexes.^{4,10,12} The $-C(O)-CHPMe_2Ph$ ligand and the U-O bond distance are quite like those in $(OC)_5WC(OUCp_3)CHPMePh_2$ ¹⁰ and $Cp(OC)_2MnC(OUCp_3)CHPMe_2Ph$ ¹² and indicate that the bonding within the ligand is similar among all three complexes. However, the U-O1-C1 angle, 171 (2)°, is larger than 158 (2)° in $(OC)_5WC(OUCp_3)CHPMePh_2$ ¹⁰ and 160 (2)° in $Cp(OC)_2MnC(OUCp_3)CHPMe_2Ph$.¹² This leads to nonbonded contacts $U\cdots HC2$, 3.8 Å, and $U'\cdots HC2'$, 3.7 Å, which are significantly longer than the corresponding distances of 3.5 and 3.4 Å for the two independent molecules of $Cp(OC)_2MnC(OUCp_3)CHPMe_2Ph$ ¹² and 3.3 Å in $(OC)_5WC(OUCp_3)CHPMePh_2$.¹⁰ The relatively small CH isotropic shift observed in the NMR spectrum of $Cp(OC)CoC(OUCp_3)CHPMe_2Ph$ is consistent with the larger U-H distances in this compound and suggests that this structural feature persists in solution.

Within $Cp(OC)CoC(OUCp_3)CHPMe_2Ph$ the Co, C1, C2, O1, and P atoms are coplanar; this plane approximately bisects the Cp(centroid)-Co-CO angle, thus minimizing steric repulsions. Some pertinent bond distances are as follows: Co-C1, 1.87 (3); Co-C6, 1.65 (5); C1-O1, 1.36 (4); C6-O6, 1.16 (6) Å. Several contributing resonance structures may be written for this molecule:



We have argued that B and C are the dominant resonance forms in complexes containing a $M-C(OUCp_3)CHPR_3$ moiety,^{10,12} and a similar conclusion has been reached for $M-C(OSiMe_3)CHPR_3$ complexes.¹⁵ However, there are very few comparison molecules to demonstrate if B and C are similarly important in $Cp(OC)CoC(OUCp_3)CHPMe_2Ph$. The most closely related complex whose structure has been determined is $Cp(OC)Co=C(OZrCp_2)(C_4H_6)$, which is described as a Fischer carbene complex with considerable Co-C multiple-bond character.¹⁶ While $Co=C$, 1.815 (4) Å, $Co-C$ (carbonyl), 1.692 (4) Å, and $C-O$ (acyl) 1.287 (4) Å in this compound cannot be distinguished at the 3σ level from analogous distances in $Cp(OC)CoC(OUCp_3)CHPMe_2Ph$, there are significant differences between the two molecules. The most obvious is that the plane defined by Co and the α -C, β -C, and O within the carbene ligand of $Cp(OC)Co=C(OZrCp_2)(C_4H_6)$ also contains the carbonyl C and O atoms. This conformation was assumed to reflect a π system extending over all these atoms. In the bonding of $Cp(OC)Co=C(OZrCp_2)(C_4H_6)$ a resonance form analogous to B is not possible. As a result, greater charge delocalization from

Co into the carbene ligand is logical in $Cp(OC)Co=C(OZrCp_2)(C_4H_6)$.

In addition to the compounds mentioned above, $CpCo(CO)_2$,¹⁷ and $(C_5Me_5)Co(CO)_2$,¹⁸ no compounds containing the $Cp(OC)Co-$ moiety, no Co(I) alkyls, and only a few cobalt Fischer carbene complexes have been structurally characterized. Within this limited set of compounds, the average Co-C1 bond length in $Cp(OC)CoC(OUCp_3)CHPMe_2Ph$, 1.87 (3) Å, can be compared with 1.902 (3) Å in $Cp(PhS)Co[C(NMe)CH_2CH_2(NMe)]$,¹⁹ 1.91 (1) Å in $(Ph_3Ge)(OC)_3CoC(COEt)(Et)$,²⁰ and 1.97 (2) Å in $(Ph_3P)(ON)Co[C(NMe)CH(Me)CH_2(NMe)]$.²¹ The Cp-Co separation, the Co-CO distance, and the C-O distances in $Cp(OC)CoC(OUCp_3)CHPMe_2Ph$ are all in the range observed in these other cobalt complexes.

An interesting feature of the crystal structure of $Cp(OC)CoC(OUCp_3)CHPMe_2Ph$ is the different packing of the two independent molecules in the asymmetric unit; a partial packing diagram is shown in Figure 2. Of particular relevance are the shortest intermolecular $U\cdots OC$ distances of 4.42 (4) Å between molecules containing U, Co, etc., compared to 3.65 (4) Å between the molecules containing the primed atoms U' , Co' , etc. As indicated by these differences, there are two distinctly different carbonyl environments within the crystal which give rise to two CO stretching modes in the IR spectrum.

Experimental Section

Reaction of $CCo(CO)_2$ with $Cp_3UCHPMeRPh$. A 0.14-mL (0.14 g, 1.0 mmol) sample of $CpCo(CO)_2$ was added to 0.60 g (1.0 mmol) of $Cp_3UCHP(Me)_2(Ph)$ dissolved in 20 mL of THF. The mixture was allowed to react, without stirring, for 4 days at room temperature. The mixture was then filtered to remove a small amount of precipitate that had formed. Volatile materials were evaporated, leaving a red-brown solid, which was washed with 2 mL of benzene followed by 10 mL of hexane and finally dried under vacuum to yield $Cp(OC)CoC(OUCp_3)CHPMe_2Ph$ in 53% yield (0.42 g). This red-brown, air- and moisture-sensitive material is soluble in THF, sparingly soluble in aromatic hydrocarbons, and insoluble in aliphatic hydrocarbons. ¹H NMR (THF-*d*₆, 25 °C) δ 15.02 (d, 1 H, $J_{PCH} = 31$ Hz, PCH), 7.83 (m, 2 H, PPh), 7.53 (m, 3 H, PPh), 1.85 (d, 6 H, $J_{PCH} = 14$ Hz, PMe), 0.37 (s, 5 H, CoCp), -9.47 (s, 15 H, UCp). IR (2100–1800 cm^{-1} , smear on NaCl plates) 1906 (s), 1860 (vs) cm^{-1} . Anal. Calcd: C, 48.70; H, 4.22. Found: C, 46.06; H, 4.67.

$Cp(OC)CoC(OUCp_3)CHPMePh_2$ can be prepared similarly. ¹H NMR (THF-*d*₆, 25 °C) δ 14.44 (d, 1 H, $J_{PCH} = 30$ Hz, PCH), 8.0 (m, 6 H, PPh), 7.5 (m, 4 H, PPh), 0.73 (d, 3 H, $J_{PCH} = 14$ Hz, PMe), -0.12 (s, 5 H, CoCp), -8.90 (s, 15 H, UCp).

Thermolysis of $Cp(OC)CoC(OUCp_3)CHPMe_2Ph$. A solution of 0.30 g (0.39 mmol) of $Cp(OC)CoC(OUCp_3)CHPMe_2Ph$ in 5 mL of THF was placed in a glass tube. This tube was sealed and heated to 90 °C for 2 days. The precipitate that formed during the heating was removed by filtration, and the solvent was evaporated to yield a dark red residue. Extraction of the residue with benzene, followed by solvent evaporation gave 0.022 g (20% yield) of red, oily $Cp(OC)Co(PMe_2Ph)$. ¹H NMR (THF-*d*₆, 25 °C) δ 7.83 (m, 2 H, PPh), 7.35 (m, 3 H, PPh), 4.67 (s, 5 H, CoCp), 1.66 (d, 6 H, $J_{PCH} = 9$ Hz, PMe). ³¹P NMR (THF-*d*₆, 25 °C) 33.09 (s, br). IR (2100–1800 cm^{-1} , smear on NaCl plates) 1910 (vs, br) cm^{-1} . Mol wt (EI Mass Spectrum) 290. These ¹H NMR, ³¹P NMR, and IR spectra are identical with those of an authentic sample of $Cp(OC)Co(PMe_2Ph)$ synthesized as described in the literature.²²

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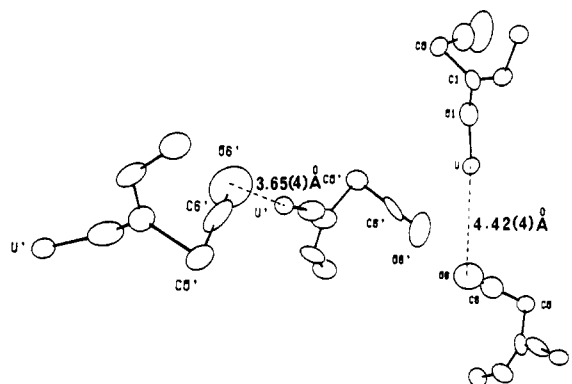
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Table I. Crystal, Data Collection, and Reduction Parameters for Cp(OC)CoC(OUCP₃)CHP(Me)₂(Ph)

formula	C ₃₁ H ₃₂ O ₂ CoPU
formula wt	764.53
space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> , Å	15.645 (2)
<i>b</i> , Å	23.828 (3)
<i>c</i> , Å	15.140 (3)
α, deg	90
β, deg	90
γ, deg	90
<i>V</i> , Å ³	5640 (2)
<i>Z</i>	8
density, g/cm ³	1.800
μ, cm ⁻¹	61.17
cryst dimen, mm	0.20 × 0.36 × 0.40
cryst shape	tetragonal
radiation	Mo Kα = 0.71073
scan type	2θ:θ
scan rate, deg/min	4–24
2θ range, deg	3–55
total observations	7186
unique observations	6348
unique data with <i>I</i> > 3σ(<i>I</i>)	3433
abs corr factor range	1.0056–3.8214
no. of parameters	294
over determination ratio	11.7
<i>R</i> ^a	0.0555
<i>R</i> _G ^b	0.0644

$$^a R = \sum (|F_o - F_c|) / \sum (F_o). \quad R_G = [\sum (|F_o - F_c|^2) \sum (F_o)^2]^{1/2}.$$

The precipitate that formed during the reaction was not soluble in aliphatic or aromatic hydrocarbons, THF, acetone, chloroform, acetonitrile, methanol, or water. An IR spectrum obtained on a Nujol mull contained no peaks between 1650 and 2500 cm⁻¹, nor did it contain a peak at 940 cm⁻¹, which would be characteristic of UO₂²⁺. No meaningful mass spectra were obtained from this solid material. Only fragments arising from CpH could be con-

**Figure 2.** Partial packing diagram of Cp(OC)CoC(OUCP₃)CHPMe₂Ph showing the intermolecular, nonbonding distances of U–O6 and U'–O6'. The Cp, Me, and Ph groups have been removed for clarity.

fidently identified in mass spectra obtained on the volatile materials formed when the precipitate was exposed to moisture. Analysis of the precipitate was C, 43.04%; H, 3.55%, which can be compared to C, 41.88%; H, 3.38% for Cp₃UOCC₃H.

Cp(OC)Co(PMePh₂) forms similarly. ¹H NMR (THF-*d*₆, 25 °C) δ 7.66 (m, 4 H, PPh), 7.37 (m, 6 H, PPh), 4.61 (s, 5 H, CoCp), 1.95 (d, 3 H, *J*_{PCH} = 9 Hz, PMe).

Collection and Reduction of X-ray Data. X-ray-quality crystals of Cp(OC)CoC(OUCP₃)CHPMe₂Ph were grown from a THF solution onto which a 1:20 toluene:pentane mixture had been layered. The dark red crystals were mounted in 0.5-mm glass capillaries and sealed under nitrogen. After examination of preliminary photographs, a crystal was selected for the subsequent diffraction study. Crystal, data collection, and refinement parameters are listed in Table I. Instrumentation, procedures, and programs used have been previously described. Cell constants were determined by least-squares methods from the centered

Table II. Positional Parameters for Cp(OC)CoC(OUCP₃)CHPMe₂Ph

atom	<i>X</i>	<i>Y</i>	<i>Z</i>	atom	<i>X</i>	<i>Y</i>	<i>Z</i>
U	0.0436 (1)	0.2743 (1)	0.4558 (1)	U'	-0.2130 (1)	0.4831 (1)	-0.1888 (1)
Co	0.2766 (3)	0.3912 (2)	0.3820 (3)	Co'	-0.0825 (2)	0.3930 (2)	0.0518 (3)
P	0.1716 (5)	0.5017 (3)	0.4995 (6)	P'	-0.1885 (5)	0.2670 (4)	-0.0044 (6)
O1	0.124 (1)	0.3431 (8)	0.439 (2)	O1'	-0.175 (1)	0.4220 (9)	-0.094 (2)
C1	0.170 (2)	0.392 (1)	0.438 (2)	O6'	-0.235 (2)	0.408 (2)	0.150 (2)
C2	0.129 (2)	0.434 (1)	0.482 (2)	C6'	-0.172 (3)	0.403 (2)	0.109 (2)
C3	0.093 (2)	0.538 (1)	0.566 (2)	C1'	-0.157 (2)	0.378 (1)	-0.043 (2)
C4	0.274 (2)	0.503 (1)	0.559 (2)	C2'	-0.202 (2)	0.331 (1)	-0.063 (2)
C6	0.322 (3)	0.374 (2)	0.475 (3)	C3'	-0.204 (3)	0.270 (2)	0.113 (2)
O6	0.352 (3)	0.362 (2)	0.542 (2)	C4'	-0.268 (2)	0.222 (1)	-0.052 (3)
C11	-0.071 (2)	0.312 (1)	0.330 (1)	C11'	-0.207 (1)	0.5984 (9)	-0.157 (1)
C12	-0.116 (2)	0.272 (1)	0.381 (1)	C12'	-0.212 (1)	0.5726 (9)	-0.072 (1)
C13	-0.129 (2)	0.294 (1)	0.467 (1)	C13'	-0.135 (1)	0.5433 (9)	-0.057 (1)
C14	-0.093 (2)	0.349 (1)	0.469 (1)	C14'	-0.082 (1)	0.5510 (9)	-0.132 (1)
C15	-0.057 (2)	0.360 (1)	0.385 (1)	C15'	-0.126 (1)	0.5850 (9)	-0.194 (1)
C21	0.110 (2)	0.301 (1)	0.622 (2)	C21'	-0.382 (1)	0.5141 (7)	-0.203 (2)
C22	0.020 (2)	0.304 (1)	0.630 (2)	C22'	-0.373 (1)	0.4978 (7)	-0.113 (2)
C23	-0.013 (2)	0.248 (1)	0.622 (2)	C23'	-0.361 (1)	0.4388 (7)	-0.111 (2)
C24	0.057 (2)	0.211 (1)	0.609 (2)	C24'	-0.362 (1)	0.4186 (7)	-0.199 (2)
C25	0.133 (2)	0.244 (1)	0.609 (2)	C25'	-0.375 (1)	0.4652 (7)	-0.256 (2)
C31	0.175 (1)	0.230 (1)	0.356 (2)	C31'	-0.068 (1)	0.454 (1)	-0.283 (2)
C32	0.151 (1)	0.187 (1)	0.416 (2)	C32'	-0.119 (1)	0.405 (1)	-0.275 (2)
C33	0.068 (1)	0.167 (1)	0.391 (2)	C33'	-0.193 (1)	0.412 (1)	-0.328 (2)
C34	0.041 (1)	0.198 (1)	0.316 (2)	C34'	-0.188 (1)	0.466 (1)	-0.369 (2)
C35	0.107 (1)	0.237 (1)	0.294 (2)	C35'	-0.111 (1)	0.492 (1)	-0.341 (2)
C41	0.314 (2)	0.3533 (7)	0.261 (2)	C41'	0.030 (2)	0.366 (1)	-0.011 (2)
C42	0.375 (2)	0.3944 (7)	0.286 (2)	C42'	0.025 (2)	0.426 (1)	-0.017 (2)
C43	0.332 (2)	0.4469 (7)	0.292 (2)	C43'	0.022 (2)	0.448 (1)	0.070 (2)
C44	0.245 (2)	0.4382 (7)	0.271 (2)	C44'	0.025 (2)	0.402 (1)	0.130 (2)
C45	0.233 (2)	0.3803 (7)	0.252 (2)	C45'	0.031 (2)	0.352 (1)	0.080 (2)
C51	0.182 (1)	0.5456 (9)	0.404 (2)	C51'	-0.090 (1)	0.232 (1)	-0.030 (2)
C52	0.256 (1)	0.5766 (9)	0.387 (2)	C52'	-0.053 (1)	0.197 (1)	0.033 (2)
C53	0.260 (1)	0.6106 (9)	0.312 (2)	C53'	0.022 (1)	0.168 (1)	0.012 (2)
C54	0.113 (1)	0.5485 (9)	0.346 (2)	C54'	0.060 (1)	0.174 (1)	-0.071 (2)
C55	0.117 (1)	0.5825 (9)	0.271 (2)	C55'	0.023 (1)	0.210 (1)	-0.133 (2)
C56	0.191 (1)	0.6135 (9)	0.254 (2)	C56'	-0.052 (1)	0.239 (1)	-0.113 (2)

Table III. Thermal Parameters for $Cp(OC)CoC(OUCp_3)CHPMe_2Ph$

Anisotropically Refined Atoms							
	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	
U	0.0375 (5)	0.0337 (4)	0.0515 (6)	0.0035 (6)	0.0057 (6)	0.0063 (5)	
Co	0.045 (2)	0.056 (2)	0.047 (2)	0.004 (2)	0.005 (2)	0.004 (2)	
P	0.053 (5)	0.050 (5)	0.059 (5)	-0.006 (4)	0.008 (4)	-0.009 (4)	
O1	0.08 (2)	0.04 (1)	0.08 (2)	-0.02 (1)	0.02 (1)	0.01 (1)	
C1	0.07 (2)	0.05 (2)	0.02 (2)	0.00 (1)	0.00 (1)	-0.01 (2)	
C2	0.06 (2)	0.03 (1)	0.07 (2)	0.00 (2)	0.02 (2)	-0.01 (1)	
C3	0.08 (2)	0.05 (2)	0.08 (3)	-0.03 (2)	0.03 (2)	0.01 (2)	
C4	0.04 (2)	0.06 (2)	0.08 (2)	0.00 (2)	-0.03 (2)	-0.01 (2)	
C6	0.09 (3)	0.10 (3)	0.08 (3)	0.00 (3)	0.00 (3)	0.02 (2)	
O6	0.17 (4)	0.22 (4)	0.08 (2)	0.03 (3)	0.01 (3)	0.09 (3)	
U'	0.0343 (4)	0.0388 (5)	0.0401 (5)	-0.0079 (6)	0.0025 (5)	-0.0035 (5)	
Co'	0.038 (2)	0.067 (3)	0.061 (3)	-0.008 (3)	-0.008 (2)	0.001 (2)	
P'	0.055 (5)	0.046 (5)	0.072 (6)	-0.001 (5)	-0.009 (4)	-0.005 (4)	
O1'	0.04 (1)	0.06 (1)	0.10 (2)	-0.02 (1)	0.00 (1)	0.00 (1)	
O6'	0.09 (2)	0.24 (4)	0.11 (3)	-0.08 (3)	0.05 (2)	0.01 (3)	
C6'	0.08 (3)	0.14 (4)	0.05 (2)	-0.06 (3)	-0.02 (2)	-0.02 (3)	
C1'	0.04 (1)	0.04 (1)	0.07 (2)	0.02 (2)	-0.02 (2)	0.01 (1)	
C2'	0.06 (2)	0.06 (2)	0.07 (2)	-0.01 (2)	-0.02 (2)	-0.02 (2)	
C3'	0.13 (3)	0.06 (2)	0.04 (2)	0.01 (2)	0.02 (2)	-0.01 (3)	
C4'	0.06 (2)	0.06 (2)	0.14 (4)	0.03 (3)	-0.05 (2)	-0.02 (2)	
Isotropically Refined Atoms							
atom	U	atom	U	atom	U	atom	U
C11	0.09 (1)	C34	0.11 (1)	C11'	0.059 (8)	C34'	0.11 (2)
C12	0.08 (1)	C35	0.09 (1)	C12'	0.065 (9)	C35'	0.10 (1)
C13	0.11 (2)	C41	0.061 (9)	C13'	0.068 (9)	C41'	0.09 (1)
C14	0.09 (1)	C42	0.07 (1)	C14'	0.07 (1)	C42'	0.07 (1)
C15	0.08 (1)	C43	0.07 (1)	C15'	0.064 (9)	C43'	0.07 (1)
C21	0.12 (2)	C44	0.09 (1)	C21'	0.060 (8)	C44'	0.10 (1)
C22	0.09 (1)	C45	0.08 (1)	C22'	0.07 (1)	C45'	0.10 (1)
C23	0.11 (2)	C51	0.09 (1)	C23'	0.053 (8)	C51'	0.062 (9)
C24	0.07 (1)	C52	0.060 (9)	C24'	0.07 (1)	C52'	0.14 (2)
C25	0.09 (1)	C53	0.07 (1)	C25'	0.058 (9)	C53'	0.13 (2)
C31	0.08 (1)	C54	0.056 (8)	C31'	0.07 (1)	C54'	0.08 (1)
C32	0.07 (1)	C55	0.08 (1)	C32'	0.10 (1)	C55'	0.09 (1)
C33	0.09 (1)	C56	0.07 (1)	C33'	0.10 (1)	C56'	0.09 (1)

Table IV. Bond Distances (Å) for $Cp(OC)CoC(OUCp_3)CHPMe_2Ph$

U-O1	2.08 (2)	U'-O1'	2.13 (2)
Co-C1	1.86 (3)	Co'-C1'	1.88 (3)
O1-C1	1.38 (4)	O1'-C1'	1.34 (4)
C2-C1	1.35 (4)	C2'-C1'	1.36 (4)
P-C2	1.77 (3)	P'-C2'	1.77 (3)
P-C3	1.81 (4)	P'-C3'	1.80 (3)
P-C4	1.84 (3)	P'-C4'	1.80 (4)
P-C51	1.79 (3)	P'-C51'	1.79 (2)
Co-C6	1.64 (5)	Co'-C6'	1.66 (4)
C6-O6	1.15 (6)	C6'-O6'	1.18 (5)
U-C11	2.77 (3)	U'-C11'	2.79 (2)
U-C12	2.74 (3)	U'-C12'	2.77 (2)
U-C13	2.75 (3)	U'-C13'	2.74 (2)
U-C14	2.78 (3)	U'-C14'	2.75 (2)
U-C15	2.79 (3)	U'-C15'	2.78 (2)
U-C21	2.80 (3)	U'-C21'	2.75 (2)
U-C22	2.76 (3)	U'-C22'	2.77 (2)
U-C23	2.74 (3)	U'-C23'	2.80 (2)
U-C24	2.77 (3)	U'-C24'	2.79 (2)
U-C25	2.81 (3)	U'-C25'	2.76 (2)
U-C31	2.76 (2)	U'-C31'	2.77 (2)
U-C32	2.74 (2)	U'-C32'	2.71 (3)
U-C33	2.76 (3)	U'-C33'	2.72 (3)
U-C34	2.79 (3)	U'-C34'	2.79 (3)
U-C35	2.79 (3)	U'-C35'	2.81 (3)
Co-C41	2.12 (2)	Co'-C41'	2.10 (3)
Co-C42	2.12 (2)	Co'-C42'	2.12 (3)
Co-C43	2.10 (2)	Co'-C43'	2.10 (3)
Co-C44	2.08 (2)	Co'-C44'	2.07 (3)
Co-C45	2.10 (3)	Co'-C45'	2.07 (3)

Table V. Bond Angles (deg) for $Cp(OC)CoC(OUCp_3)CHPMe_2Ph^a$

C1-Co-C6	90 (2)	C1'-Co'-C6'	84 (2)
C3-P-C2	106 (1)	C3'-P'-C2'	117 (2)
C4-P-C2	114 (1)	C4'-P'-C2'	103 (2)
C4-P-C3	108 (2)	C4'-P'-C3'	109 (2)
C51-P-C2	116 (1)	C51'-P'-C2'	113 (1)
C51-P-C3	103 (1)	C51'-P'-C3'	110 (2)
C51-P-C4	108 (1)	C51'-P'-C4'	104 (1)
C1-O1-U	171 (2)	C1'-O1'-U'	171 (2)
O1-C1-Co	117 (2)	O1'-C1'-Co'	115 (2)
C2-C1-Co	131 (2)	C2'-C1'-Co'	130 (2)
C2-C1-O1	111 (3)	C2'-C1'-O1'	114 (3)
C1-C2-P	124 (2)	C1'-C2'-P'	122 (2)
O6-C6-Co	178 (4)	O6'-C6'-Co'	178 (4)
Cp1-U-Cp2	116 (1)	Cp1'-U-Cp2'	116 (1)
Cp2-U-Cp3	119 (1)	Cp2'-U-Cp3'	118 (1)
Cp3-U-Cp2	119 (1)	Cp3'-U-Cp2'	119 (1)
O1-U-Cp1	99 (1)	O1'-U-Cp1'	99 (1)
O1-U-Cp2	99 (1)	O1'-U-Cp2'	101 (1)
O1-U-Cp3	102 (1)	O1'-U-Cp3'	97 (1)

^aCp represents the centroid of a cyclopentadienide ring.

The coordinates of a uranium atom were determined by using MULTAN80.²⁴ Least-squares refinement of this uranium using SHELX-76²⁵ gave an error index of $R = 0.3763$; at this point a difference Fourier map revealed a second uranium position.

(23) PROCESS, a computer program for Lorentz polarization and empirical absorption correction of diffraction data, obtained from Prof. R. Bau, University of Southern California, and modified by M. Carrie, University of Hawaii, 1986.

(24) MULTAN80, a system of computer programs for the automatic solution of crystal structure from X-ray diffraction data by P. Main, 1980.

(25) SHELX-76, a system of computer programs for X-ray structure determination by G. M. Sheldrick, 1976.

angular coordinates of 15 intense reflections with 2θ values between 31° and 38° . The diffraction data were corrected for absorption by using PROCESS.²³

Subsequent refinement of the two uraniums converged to $R = 0.2067$. The positions of the remaining atoms were obtained in a straightforward fashion from difference maps after several subsequent cycles of refinement. In the final cycles all atoms were refined anisotropically, except for the Cp and Ph rings, which were treated as rigid groups by using the parameters contained in SHELX-76. In the last cycle of refinement, no parameter shifted more than 23% of its standard deviation with $R = 0.0555$ and $R_G = 0.0644$. The final difference map showed maximum peaks of $1.41 \text{ e}/\text{\AA}^3$ at 0.95 \AA from uranium. Refinement of the enantiomeric structure gave $R = 0.072$ and $R_G = 0.0792$, thus confirming the absolute configuration of the molecule.

Final positional parameters and thermal parameters are listed in Tables II and III, respectively. Bond distances are summarized in Table IV, and bond angles in Table V. Bond angles and

distances, but not torsional angles, between the two independent molecules contained in the asymmetric unit are indistinguishable; an ORTEP drawing of one of these is shown in Figure 1.

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Supplementary Material Available: Observed and calculated structure factors for $\text{Cp}(\text{OC})\text{CoC}(\text{OUCp}_3)\text{CHPMe}_2\text{Ph}$ (16 pages). Ordering information is given on any current masthead page.

Interaction of Monohydrido Complexes of Rhodium(I) with 1-Alkynes. Experimental Study on Deceptively Simple Reactions

Claudio Bianchini,* Andrea Meli, Maurizio Peruzzini, and Francesco Vizza

Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione, ISSECC CNR, Via J. Nardi 39, 50132 Firenze, Italy

Piero Frediani

Dipartimento di Chimica Organica, Università degli Studi di Firenze, Firenze, Italy

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The reaction of $\text{HC}\equiv\text{CR}$ ($\text{R} = \text{CO}_2\text{Et}$, Ph, $n\text{-C}_3\text{H}_7$, $n\text{-C}_5\text{H}_{11}$, SiMe_3) with the Rh(I) monohydrides $[(\text{NP}_3)\text{RhH}]$ (**1**) and $[(\text{PP}_3)\text{RhH}]$ (**2**) in THF is influenced by a number of factors, including stoichiometry, alkyne substituent, and temperature ($\text{NP}_3 = \text{N}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$; $\text{PP}_3 = \text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$). At room temperature, $\text{HC}\equiv\text{CCO}_2\text{Et}$ and $\text{HC}\equiv\text{CPh}$ react with an equimolar amount of **1**, yielding mixtures of the trigonal-bipyramidal complexes $[(\text{NP}_3)\text{Rh}(\text{C}\equiv\text{CR})]$ and $[(\text{NP}_3)\text{Rh}\{\textit{E}\text{-CH}=\text{C}(\text{H})\text{R}\}]$ ($\text{R} = \text{CO}_2\text{Et}$, Ph). The σ -acetylide compounds form via C(alkyne)-H oxidative addition to rhodium, followed by H_2 elimination. For $\text{R} = \text{alkyl}$ and SiMe_3 , no reaction occurs even when a 10-fold excess of 1-alkyne is used. In contrast, by treatment of **1** with an excess of $\text{HC}\equiv\text{CCO}_2\text{Et}$, the σ -acetylide complex selectively forms together with ethyl acrylate. At reflux temperature, **1** reacts with a 10-fold excess of 1-alkynes to give σ -acetylide derivatives ($\text{R} = \text{SiMe}_3$, CO_2Et) or σ -acetylide/ σ -alkenyl mixtures ($\text{R} = \text{alkyl}$, Ph). A variety of organic products is also formed, including as the major products 1,3,5- and 1,2,4-trisubstituted benzenes, 1,4-butadiynes, and butenynes. The only 1-alkyne that stoichiometrically reacts with **2** in THF at room temperature is $\text{HC}\equiv\text{CCO}_2\text{Et}$. As a result, the σ -alkenyl $[(\text{PP}_3)\text{Rh}\{\textit{gem}\text{-C}(\text{CO}_2\text{Et})=\text{CH}_2\}]$ is obtained. The σ -acetylide complexes $[(\text{PP}_3)\text{Rh}(\text{C}\equiv\text{CR})]$ ($\text{R} = \text{CO}_2\text{Et}$, Ph) are synthesized by reacting **2** with a 10-fold excess of the corresponding 1-alkyne. No reaction is observed for $\text{R} = \text{alkyl}$ and SiMe_3 . When performed in refluxing THF, the reactions between **2** and an excess of 1-alkyne lead to the formation of σ -acetylide complexes regardless of the alkyne substituent. Again, the reactions are catalytic and cause extensive conversion of 1-alkynes to a variety of linear and cyclic oligomers. The product distribution is essentially similar to that observed for the NP_3 hydride **1**. The stereospecific addition of 1-alkynes to either **1** or **2** is interpreted in terms of a concerted mechanism.

Introduction

The result of a reaction between a terminal alkyne and a transition-metal monohydrido complex is hardly predictable because of the number and variety of the factors that may affect the process. Besides external parameters such as temperature, solvent, and stoichiometry, one has to consider that the course of the reaction much depends also on the polyfunctional nature of both the alkyne and

the metal-hydrogen bond. The ability of C-H oxidative addition to the metal center¹ coupled with susceptibility to insert across the M-H bond² make terminal alkynes

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