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Reactions of the Tungsten Carbonyl η^2-Tritylallene Complex: Crystal Structure of Two Allene Complexes

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Summary: Reactions of cationic tungsten η^2-tritylallene complex $[Cp(CO)_3W(\eta^2\text{-}CH_2{=}C{=}CHCPh_3)]BF_4$, 1 ($Cp = \eta^5\text{-}C_5H_5$, $Ph = C_6H_5$), with $PhCH_2NHLi$ and NaN_3 give $Cp(CO)_2W[\eta^3\text{-}CH_2C(CONHCH_2Ph)CHCPh_3]$, 2, and cis-$Cp(CO)_2W(NCO)(\eta^2\text{-}CH_2{=}C{=}CHCPh_3)$, 3, respectively. In the reaction of 3 with CF_3COOH the NCO ligand is replaced, giving cis-$Cp(CO)_2W(OCOCF_3)(\eta^2\text{-}CH_2{=}C{=}CHCPh_3)$, 4. The structures of 3 and 4 have been determined by X-ray diffraction studies.

Introduction

The physical and chemical properties of transition-metal allene complexes have been studied for decades.[1] Reviews[2] have appeared in the literature. Depending upon the C═C═C substitution pattern, a diverse array of linkage isomers and stereoisomers is possible. We have recently reported electrophilic addition of a triphenylmethyl carbocation (trityl) $(C_6H_5)_3CBF_4$ to the terminal carbon of the propargyl group in $CpW(CO)_3CH_2C{\equiv}CH$, giving a π-allene complex, $Cp(CO)_3W(\eta^2\text{-}CH_2{=}C{=}CHCPh_3)BF_4$, 1. On the basis of known chemistry, there are several possible reaction types for the reaction of 1 with nucleophiles. The allene moiety could be displaced by the incoming nucleophile if it is only loosely bound. On the other hand, nucleophilic attack could take place at two possible sites, namely, the allene and/or CO ligands. In cationic iron complexes,[3] nucleophilic addition to a carbonyl ligand occurs only when an effective alternative acceptor center is not available. Indeed, in the cyclization reaction of the trityl substituted π-allene ligand of 1 the first step involves an intramolecular nucleophilic attack of a phenyl group to the terminal carbon of the allene ligand. This reaction produced two dihydronaphthalene compounds.[4] In this paper, we report another mode of nucleophilic attack giving different types of products.

Experimental Section

General Procedures. All manipulations were performed under nitrogen using vacuum line, drybox, and standard Schlenk techniques. NMR spectra were recorded on Bruker AM-300WB and AC-300 NMR spectrometers and are reported in units of parts per million with residual protons in the solvent as the internal standard ($CDCl_3$, δ 7.24). IR spectra were measured on a Perkin-Elmer 983 instrument, and frequencies (cm^{-1}) were assigned relative to a polystyrene standard. Electron impact mass spectra were determined with a Finnagan TSQ-46C spectrometer, and FAB spectra, with JEOL spectrometer. Diethyl ether was distilled from CaH_2 and stored over molecular sieves prior to use. CH_2Cl_2 was distilled from CaH_2. Benzene and THF were distilled from sodium–benzophenone. All other solvents and reagents were reagent grade and used without further purification. $W(CO)_6$ was purchased from Strem Chemical, propargyl bromide, benzylamine, NaN_3, and CF_3COOH were purchased from Merck, and $HC{\equiv}CCH_2Br$ was distilled in a small quantity before use. Complexes $[CpW(CO)_3]_2$,[5] $CpW(CO)_3CH_2\text{-}C{\equiv}CH$, 1,[6] and $[CpW(CO)_3(\eta^2\text{-}CH_2{=}C{=}CHCPh_3]BF_4$[4] were prepared according to the literature methods.

Reaction of the Tungsten (Triphenylmethyl)allene Cation with Lithium Benzylamide. A sample of 1 (0.49 g, 0.64 mmol) was dissolved in 20.0 mL of THF at −20 °C. A cold THF solution of lithium benzylamide (0.1 M, 20 mL) was added via syringe over 10 min, and the resulting mixture was stirred for 40 min at −20 °C. The solution was warmed to room temperature, and the solvent was removed under vacuum; then 2 × 30 mL of hexane was added to the crude product, and the extract was filtered. The product in the filtrate was further recrystallized from a mixture of hexane/CH_2Cl_2 to give $Cp(CO)_2W[\eta^3\text{-}CH_2C\text{-}(CONHCH_2C_6H_5)CHCPh_3]$, 2 (0.39 g), in 77% yield. Spectroscopic data for **2**: IR (cm^{-1}, CH_2Cl_2) 1949 (s), 1866 (s), 1642 (s, $\nu(C{=}O)$); ^1H NMR (20 °C, $CDCl_3$) δ 7.33, 7.16 (m, 20H, phenyl CH), 6.35 (br, NH), 5.53 (br, $CHCPh_3$), 5.28 (br, 5H, Cp), 4.45 (AB, 2H, $J_{H-H} = 14.4$ Hz, NCH_2); 2.89 (br, s, syn-CH_2), 0.10 (br, s, 1H, anti H of CH_2); (at- 30 °C exo and endo forms were observed in $CDCl_3$) exo form δ 7.24 (m, 20H, phenyl CHs), 6.64 (br, NH), 5.63 (br, $CHCPh_3$); 5.27 (br, 5 H, Cp), 4.45, 4.35 (m, NCH_2), 2.82 (br, syn-CH_2), −0.26 (br, 1H, anti H of CH_2); endo form δ 7.24 (m, 20H, phenyl CHs), 6.42 (br, NH), 5.38 (br, $CHCPh_3$), 5.26 (br, 5H, Cp), 4.45, 4.35 (m, NCH_2), 2.65 (br, syn-CH_2), 0.85 (br, 1H, anti H of CH_2). ^{13}C NMR (25 °C, $CDCl_3$) δ 223.7, 222.1 (CO), 173.8 (C═O), 146.9, 138.2, 130.3–125.9 (phenyl carbon), 93.7 (Cp), 67.5 ($\underline{C}CON$), 60.6 (CPh_3), 59.4 (CH), 36.7 ($={CH_2}$). MS, FAB: 723 ($\overline{M}^+$), 695 ($M^+ - CO$), 667 ($M^+ - 2CO$). Anal. Calcd: C, 61.59; H, 5.44; N, 1.94. Found: C, 61.46; H, 5.65; N, 1.91.

Reaction of the Tungsten (Triphenylmethyl)allene Cation with Sodium Azide. A sample of 1 (1.50 g, 2.13 mmol) was dissolved in 40.0 mL of CH_3CN at −20 °C. Addition of an aqueous solution of sodium azide (NaN_3 0.4 g in 10 mL of H_2O) via syringe caused the formation of an orange precipitate and the resulting mixture was stirred for 15 min and slowly warmed to room temperature. Then, CH_2Cl_2 (30 mL) and H_2O (15 mL) were added to dissolve the solid product and the organic layer was separated from the aqueous layer. Evaporation of solvent from the organic layer, which has been dried over $MgSO_4$, gave a crude product, $Cp(CO)_2W(NCO)(\eta^2\text{-}CH_2{=}C{=}CHPh_3)$, 3 (1.19 g), in 89% yield. Recrystallization from CH_2Cl_2 gave organe crystals of 3 for X-ray analysis. Spectroscopic data for **3**: IR (cm^{-1}, CH_2Cl_2) 2235 (m, $\nu(N{=}C{=}O)$), 2021 (vs), 1952 (s, $\nu(CO)$), 1594 (m, $\nu(C{=}C{=}C)$);

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^{1}H NMR ($CDCl_3$) δ 7.55 (dd, J_{H-H} = 3.3, 3.4 Hz, =CH), 7.41, 7.20 (m, 15H, phenyl CH), 5.49 (s, 5H, Cp), 2.38 (dd, 1H, J_{H-H} = 7.0, 3.3 Hz, one of CH_2), 1.63 (dd, J_{H-H} = 7.0, 3.4 Hz, one of CH_2); ^{13}C NMR (25 °C, $CDCl_3$) δ 219.6, 208.3 (CO), 166.1 (=C=), 133.1 (CH), 146.6, 130.5, 127.8, 126.2 (phenyl carbon), 91.4 (Cp), 65.2 (CPh_3), 59.9 (CH), 11.6 (=CH_2). MS, FAB: 629 (M^+), 587 (M^+ − NCO), 559 (M^+ − NCO, CO), 531 (M^+ − NCO, 2CO). Anal. Calcd: C, 57.25; H, 3.68. Found: C, 57.10; H, 3.45.

Reaction of Complex 3 with CF_3COOH. A sample of **3** (0.01 g, 0.15 mmol) was suspended in 20 mL of CH_2Cl_2 at 0 °C. CF_3COOH (neat, 20 μL) was added via syringe, and the resulting mixture was stirred overnight at 0 °C. After removal of all volatile substances in vacuo, 5 mL of CH_2Cl_2 and 15 mL of hexane were added to the crystalline residue under nitrogen. Dark red solids were filtered out. The solvent of the filtrate was removed under vacuum to give the crude product $Cp(CO)_2W(OCOCF_3)(\eta^2\text{-}CH_2{=}CH_2{=}CHPh_3)$, **4** (0.084 g, 74% yield). Recrystallization from CH_2Cl gave pure dark orange crystals of **4** for diffraction analysis. Spectroscopic data for **4**: IR (cm^{-1}, CH_2Cl_2) 2027 (vs), 1958 (vs), 1695 (s, ν(C=O)); ^{1}H NMR (25 °C, $CDCl_3$) δ 7.67 (dd, J_{H-H} = 3.5, 3.7 Hz), 7.29–7.05 (m, 15H, phenyl CH), 5.55 (s, 5H, Cp), 2.54 (dd, 1H, J_{H-H} = 7.7, 3.7 Hz, CH_2), 1.64 (dd, 1H, J_{H-H} = 7.7, 3.5 Hz, anti H of CH_2); ^{13}C NMR (25 °C, $CDCl_3$) δ 177.2 (C=O), 168.3 (=C=), 134.3 (=C–), 146.3, 130.4, 127.7, 126.2 (phenyl carbon), 92.2 (Cp), 65.8 (CPh_3), 13.9 (=CH_2). MS, FAB: 703 (M^+), 675 (M^+ − CO), 647 (M^+ − 2CO). Anal. Calcd: C, 53.16; H, 3.31; Found: C, 53.45; H, 3.30.

Thermolysis of Complex 3. This experiment was carried out in a NMR tube. A sample of **3** (0.02 g, 0.03 mmol) was dissolved in 0.7 mL of C_6D_6, and the solution was heated to 60 °C and turned cloudy in 30 min. The solution was further heated for 24 h. The free tritylallene was observed in ca. 60% yield (from NMR integration), and the metal part gave an unidentified product which displays a Cp resonance at δ 4.36. This metal compound decomposes in our attempt at purification. Mp of $CH_2{=}C{=}CHC(C_6H_5)_3$: 98.5–99.0 °C (uncorrected). Spectroscopic data for $CH_2{=}C{=}CHC(C_6H_5)_3$: IR (cm^{-1}, KBr) 1958 (m, allene); ^{1}H NMR ($CDCl_3$) δ 7.27, 7.14 (m, 15H, Ph), 6.26 (t, J_{H-H} = 6.6 Hz, 1H, CH), 4.72 (d, 2H, J_{H-H} = 6.6 Hz, =CH_2); ^{13}C NMR ($CDCl_3$) δ 208.3 (=C=), 146.2, 129.9, 127.6, 125.4 (Ph), 100.4 (=CH), 78.2 (=CH_2), 58.8 (CPh_3). MS, FAB: 282 (M^+), 283 (M^+ + 1). Anal. Calcd for $C_{22}H_{18}$: C, 93.57; H, 6.42. Found: C, 93.50; H, 6.50.

Reaction of Complex 3 with PPh_3. A sample of **3** (0.02 g, 0.03 mmol) was dissolved in 20 mL of CH_2Cl_2 at room temperature. PPh_3 (0.016 g, 0.06 mmol in 5 mL of CH_2Cl_2) was added, and the resulting mixture was stirred at room temperature for 24 h. After removal of all volatile substances in vacuo, 5 mL of CH_2Cl_2 and 15 mL of hexane were added to the crystalline residue. Yellow solids were filtered out to give $Cp(CO)_2W(NCO)(PPh_3)$, **5** (0.014 g), in 76% yield. The solvent of the filtrate was removed under vacuum to give $CH_2{=}C{=}CHPh_3$ (contaminated with PPh_3). Recrystallization of **5** from CH_2Cl_2 gave a pure yellow product. Spectroscopic data for **5**: IR (cm^{-1}, CH_2Cl_2) 2241 (vs, ν(N=C=O)), 1948 (vs), 1858 (s, ν(C=O)). ^{1}H NMR (25 °C, $CDCl_3$) δ 7.32–7.15 (m, 15H, phenyl CH), 5.50 (s, 5H, Cp); ^{13}C NMR (25 °C, $CDCl_3$) δ 206.8 (CO), 147.2, 130.3, 127.2, 125.9 (phenyl carbon), 92.2 (Cp); ^{31}P NMR ($CDCl_3$) δ 25.15 (J_{W-P} = 258.0 Hz). MS, FAB: 583 (M^+ − CO), 569 (M^+ − NCO), 555 (M^+ − 2CO). Anal. Calcd: C, 51.25; H, 3.31. Found: C, 51.29; H, 3.09.

X-ray Analysis of 3 and 4. Single crystals of **3** and **4** suitable for an X-ray diffraction study were grown by the methods described in the previous section. The diffraction data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer equipped with graphite monochromated Mo Kα (λα = 0.710 37 Å) radiation. The raw intensity data were converted to structure factor amplitudes and their esd's after correction for scan speed, background, Lorentz, and polarization effects. An empirical absorption correction, based on the azimuthal scan data, was applied to the data. Crystallographic computations were carried out on a Microvax III computer using the NRCC-SDP-VAX structure determination package.[7]

Table 1. Crystal and Intensity Collection Data for $CpW(CO)_2(NCO)[CH_2{=}C{=}CHCPh_3]$, 3 and $CpW(CO)_2(OCOCF_3)[CH_2{=}C{=}CHCPh_3]$, 4 (Ph = C_6H_5)

molecular formula	$C_{30}H_{23}O_3NW$, 3	$C_{31}H_{23}O_4F_3W$, 4
space group	*C*2/*c*	*C*2/*c*
a/Å	37.177(8)	41.663(6)
b/Å	8.123(2)	8.022(2)
c/Å	15.878(4)	16.187(2)
β/deg	91.31(2)	100.41(1)
V/Å^3	4794(2)	5321(1)
Z	8	8
cryst dimens/mm^3	0.05 × 0.10 × 0.25	0.10 × 0.20 × 0.40
radiation, λ/Å	Mo Kα, 0.7093	
F(000)	2375	2735
2θ range/deg	2–45.0	2–50.0
scan type (speed/deg min^{-1})	2θ/θ (2.06–8.24)	
total no. of reflns	3123	4682
no. of unique reflns $I > 2\sigma(I)$	1631	3546
no. of atoms and params	58/317	62/353
abs corr, μ/cm^{-1}	49.49	44.88
	0.825–1.000	0.763–1.000
R	0.044	0.031
R_w	0.036	0.030
GOF	1.22	1.40
Δ*F*(e/Å^3 in final map)	−0.860, 1.060	−0.800, 0.720

A suitable single crystal of **3** was mounted on the top of a glass fiber with glue. Initial lattice parameters were determined from 25 accurately centered reflections with 2Θ values in the range from 19.02 to 26.24°. Cell constants and other pertinent data are collected in Table 1. Data were collected using the Θ–2Θ scan method. The final scan speed for each reflection was determined from the net intensity gathered during an initial prescan and ranged from 2 to 7° min^{-1}. The Θ scan angle was determined for each reflection according to the equation $A + B \tan \Theta$ for which *A* and *B* were set at the values of 0.75 and 0.35, respectively. Three check reflections were measured every 30 min throughout the data collection and showed no apparent decay. Merging equivalent and duplicate reflections gave a total of 3123 unique measured data in which 1623 were considered observed, $I > 2\sigma(I)$. The structure was first solved by using the heavy atom method (Patterson synthesis) which revealed the positions of metal atoms. The remaining atoms were found in a series of alternating difference Fourier maps and least-squares refinements. The quantity minimized by the least-squares program was $w(|F_o| - |F_c|)^2$, where *w* is the weight of a given operation. The analytical forms of the scattering factor tables for the neutral atoms were used.[8] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculations in their expected positions on the basis of idealized bonding geometry but were not refined in least squares. The final residuals of this refinement were *R* = 0.030 and R_w = 0.028. The procedures for **4** were similar to those for **3** and the final residuals of this refinement were *R* = 0.030 and R_w = 0.028. The pertinent data for **3** and **4** are listed in Table 1.

Results and Discussion

Carbon–Carbon Bond Formation of the π-Allene Complex. Treatment of the cationic complex **1** with $LiNHCH_2C_6H_5$ affords the coupling product $Cp(CO)_2W(\eta^3\text{-}CH_2C(CONHCH_2C_6H_5)CHPh_3)$, **2**, in 77% yield; see Scheme 1. Complex **2** is only sparingly soluble in $CDCl_3$ and insoluble in most nonpolar solvents. The reaction proceeds via a nucleophilic attack of the amide at the cis-terminal CO followed by a C–C coupling of the resulting carbamoyl group with the center carbon of the coordinated allene ligand, yielding the η^3-allylic complex **2**. It is

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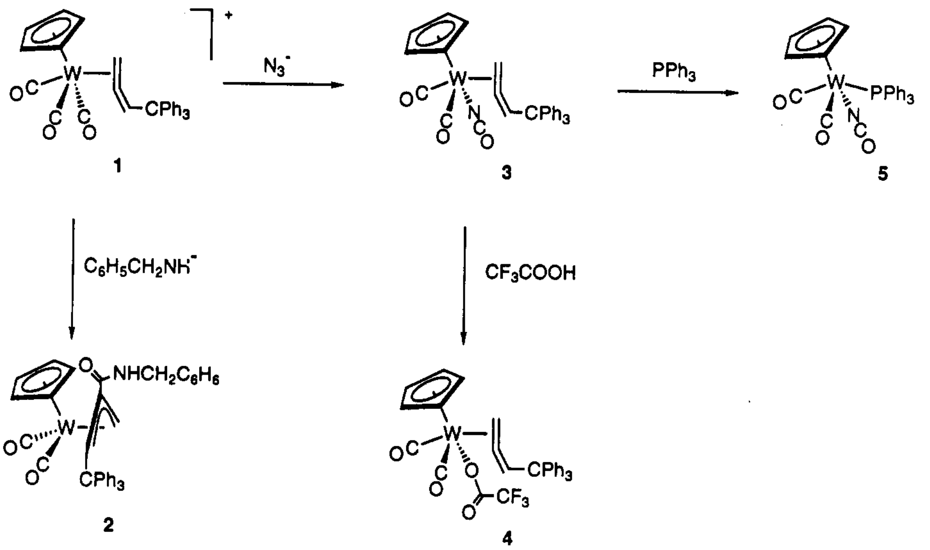
Scheme 1



necessary to keep the reaction temperature at or below −20 °C. If the reaction is carried out at a higher temperature, decomplexation of the allene ligand yields free (1-triphenylmethyl)allene and some unidentified products.

The IR spectrum of 2 shows two strong ν_{CO} vibrations at 1949 and 1866 cm^{-1} with approximately equal intensity, characteristic of a $CpW(CO)_2$ moiety, and a medium intensity absorption at 1642 cm^{-1} assignable to the $\nu_{C=O}$ of the amide group. The three allylic protons of the α-trityl-β-amido substituted allylic ligand are inequivalent. In the ^1H NMR spectrum of 2 at room temperature, the characteristic allylic resonances are observed at δ 5.53, 2.89, and 0.10, and all display a broad singlet pattern indicating a weakly coupled three spin system. In the ^{13}C NMR spectrum of 2, resonances at δ 223.7, 221.1, and 173.8 were assigned to the two metal carbonyls and the amido carbonyl, and a resonance at δ 60.6 was assigned to the carbon atom bound to three phenyl groups. A DEPT-135 experiment aided the assignment of the remaining signals. Positive peaks at δ 59.4 and in the δ 147–120 region were assigned to the allylic CH and aromatic CH carbons, respectively, and the two inverted peaks at δ 44.13 and 36.7 were assigned to the CH_2 carbons of the amido group and of the π-allyl ligand, respectively. At −30 °C both endo and exo isomers are observed in the ^1H NMR spectrum. It has been noted that the α-substituted allylic complex containing a Cp ligand generally adopts the exo conformation and the β-substituted allylic complex prefers the endo conformation.[9] We have synthesized several α-substituted allylic complexes from the reaction of a σ-allenyl complex of W with nucleophiles and found that the molecule does adopt the exo conformation. Complex 3 is an α,β-substituted complex; thus it is reasonable to see both conformations.

The reaction of the tungsten propargyl complex $Cp(CO)_3WCH_2C{\equiv}CH$ with ethanol also gave the allylic complex with a carboethoxyl group at the β-carbon of the allylic group. The reaction is believed to take place via protonation at the terminal carbon of the propargyl group.[10] In fact the iron allene complex from the protonation reaction has been characterized.[11] Our results confirm that the electrophilic addition to the terminal alkyne should take place prior to the nucleophilic attack. The σ-allenyl complex of $Cp(CO)_3WCH{=}C{=}CH_2$ displays different regiospecificity for the C—C bond formation. The reaction of the σ-allenyl complex with amine produced a product where the C—C bond formation occurs at the α-carbon.[12]

Reactions of the π-Tritylallene Complex with Azide. Reaction of 1 with NaN_3 was carried out in water at a low temperature and gave a red crystalline product, an η^2-allene complex with an isocyanate NCO ligand, $Cp(CO)_2W(NCO)(\eta^2\text{-}CH_2{=}C{=}CHCPh_3)$, 3. It is also necessary to keep the temperature below −20 °C. Complex 3 is soluble in polar solvents such as THF, $CHCl_3$, CH_3CN, and CH_2Cl_2 and not soluble in nonpolar solvents like hexane and benzene. In this reaction, nucleophilic attack occurs regiospecifically at one of the two cis CO's but not at the coordinating allene ligand. The resulting intermediate then rearranges with loss of N_2 to form an isocyanate product before C—C coupling. This reaction generates exclusively the cis complex. No trans product is observed.

The cis configuration of the two CO ligands was established by the inequivalent methylene protons, as indicated by the separated resonances at δ 2.38 and 1.63 in the ^1H NMR spectrum of 3 as well as the inequivalent CO's (δ 219.6 and 208.3). The IR spectrum of 3 exhibits the two strong ν_{CO} vibrations associated with the cis geometry of the piano stool structure as well as one strong ν_{NCO} in the expected range 2242–2233 cm^{-1}. The synthesis of the isocyanate ligand by different methods has been reported.[13] Under photolytic conditions the nitrosyl ligand of $Cp(CO)Mo(PPh_3)(NO)$ was converted to nitrene by PPh_3. Subsequent coupling of the nitride ligand with CO led to formation of the isocyanate ligand. Although the isocyanate complex has been observed to form from coupling of coordinated nitrene with CO, this process is less likely to occur in our reaction, since coordination of

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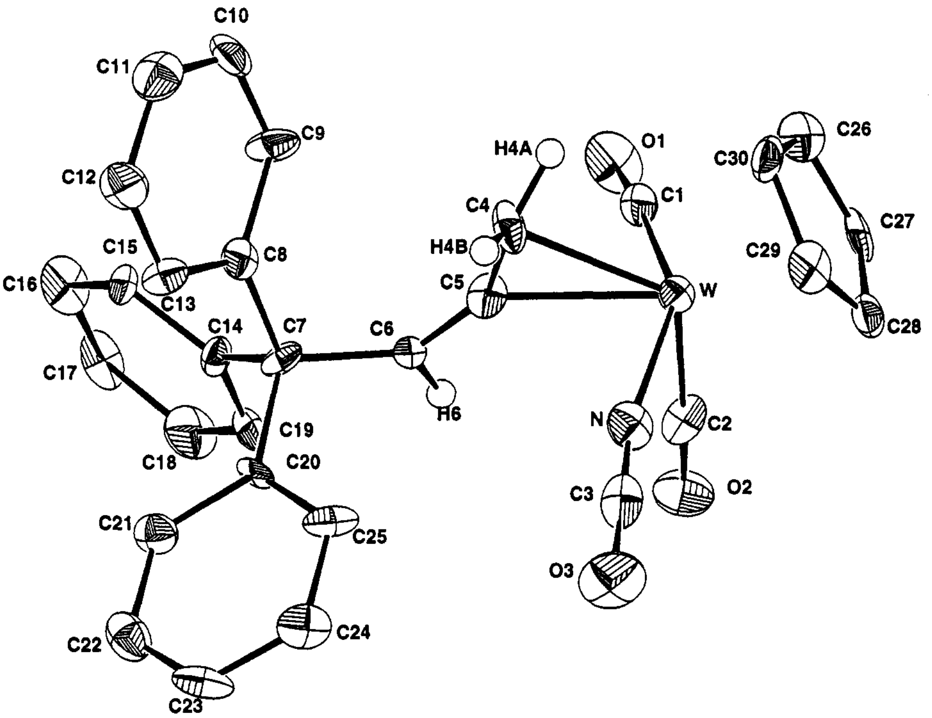

Figure 1. ORTEP drawing of 3 with thermal ellipsoids shown at the 30% probability level.

the azide ligand would require dissociation of one CO or the allene ligand.

Treatment of complex 3 with trifluoroacetic acid affords the allene complex with a monodentate trifluoroacetate ligand, $Cp(CO)_2W(OCOCF_3)(\eta^2\text{-}CH_2{=}C{=}CHCPh_3)$, 4. This result is consistent with those reported for the reactions of both the cationic rhenium[14] and the neutral manganese[15] isocyanate complexes with formic acid, which also gave the formate complexes. The ^1H NMR spectrum of 4 exhibits a Cp resonance at δ 5.55, three olefin resonances at δ 7.67, 2.54, and 1.64, and the expected phenyl resonances. In the ^{13}C NMR spectrum of 4, a resonance at δ 13.9 (which gave an inverted peak in a DEPT-135 experiment) was assigned to the terminal, coordinated carbon of the allene ligand ($=CH_2$). Similar upfield ^{13}C NMR shifts were observed for the coordinated methylene carbons of 3 (δ 11.6) and other allene complexes.

Thermolysis of 3 at 60 °C gives free tritylallene, $CH_2{=}C{=}CHCPh_3$, as the major product. Possibly because of lack of positive charge, the coordinated tritylallene ligand of 3 did not undergo cyclization. The organometallic fragments, even though with only one Cp resonance, cannot be identified. Thermolysis of complex 3 at room temperature in the presence of PPh_3 afforded the substituted complex $Cp(CO)_2W(NCO)(PPh_3)$, 5, and free tritylallene. The allene ligand is replaced by PPh_3. The ^1H NMR spectrum of 5 exhibits a singlet Cp resonance at δ 5.50, indicating the cis configuration of the NCO and PPh_3 ligands. In the ^{13}C NMR spectrum of 5, a resonance at δ 92.2 was assigned to the Cp ligand.

The carbon—carbon formation between the donor atoms of adjacent acyl and alkenyl ligands has been reported.[16] In the presence of base, 1 is converted, with no carbon—carbon bond formation, to an alylic complex $Cp(CO)_2W[\eta^3\text{-}(Ph_3C)HCCHCH_2]$, as the minor product.[17] The major product of this reaction is $Cp(CO)_2W(\eta^3\text{-}CH_2C(COOH)\text{-}CHCPh_3)$, which can also be obtained from the reaction of H_2O with 1. Protonation of $Fe(CO)_4(\eta^2\text{-}CMe_2{=}C{=}CMe_2)$ with HBF_4 in acetic anhydride occurred at the central carbon, giving the cationic π-allyl complex, which was readily converted into the conjugated diene complex by loss of a CO.[18] The most common reaction of cationic π-allene complexes is the addition of a nucleophile to the terminal carbon. Thus addition of $NaBH_4$,Et_2NH, and PPh_3 to $Cp(CO)_2Fe(CH_2{=}C{=}CHR)^+$ yielded isolable metal vinyl products. However, addition of NaN_3, $PhNH_2$, and $P(OMe)_3$ afforded unstable impure complexes.[19] Reaction of the $Cp(CO)_2Fe(\eta^2\text{-}CH_2{=}CH_2)$ cation with NaN_3 was first reported[20] to yield isocyanate complex $CpFe(CO)(NCO)(\eta^2\text{-}CH_2{=}CH_2)$ and was later found to give ligand displacement product $CpFe(CO)_2N_3$.[21] It is therefore interesting to find tht the π-allene ligand in our tungsten complexes is relatively inert.

X-ray Crystal Structure of Two Allene Complexes. Complexes 3 and 4 are rare examples of four leg piano stool metal allene complexes. The two ORTEP drawings of 3 and 4 are shown in Figures 1 and 2, respectively. Both complexes display piano stool coordination geometry about the metal atom. Some selected bond distances and angles are shown in Tables 2 and 3. The W(CO) and $W(C_5H_5)$ distances and angles are normal. The π-allene ligand is cis to the isocyanate ligand in 3 and also cis to the trifluoroacetate ligand in 4. The most interesting feature of 3 and 4 is the bound isocyanato and allene ligands. Interestingly, the C—C vector of the coordinated allene double bond is approximately perpendicular to the cy-

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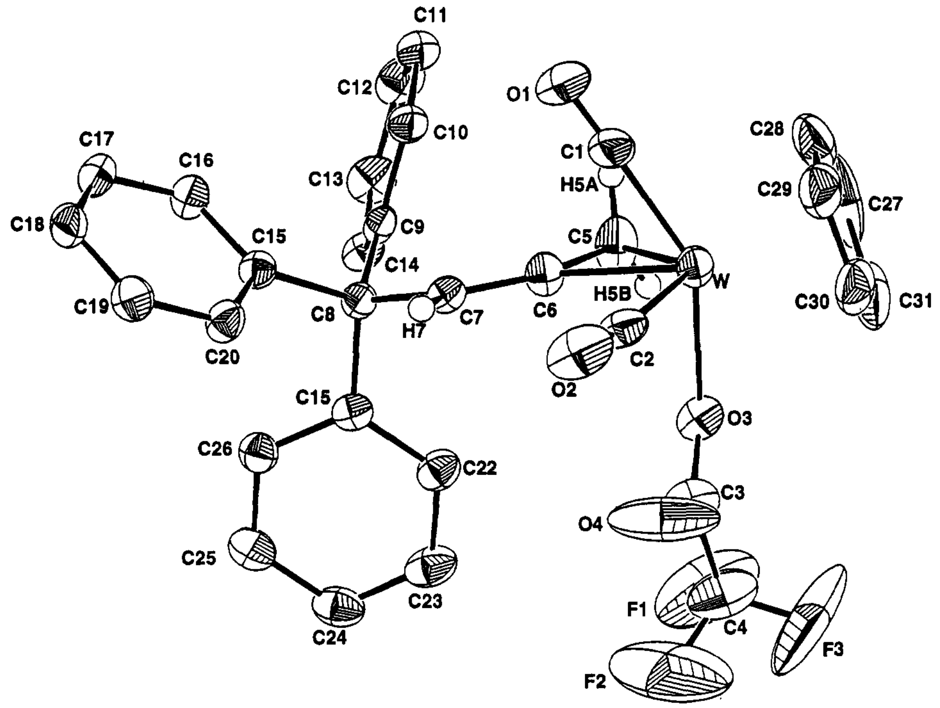

Figure 2. ORTEP drawing of 4 with thermal ellipsoids shown at the 30% probability level.

Table 2. Selected Bond Distances (Å) for Complexes 3 and 4

complex 3		complex 4	
W-C(1)	2.000(15)	W-C(1)	1.995(7)
W-C(2)	1.969(19)	W-C(2)	1.994(6)
W-C(4)	2.242(15)	W-C(5)	2.229(6)
W-C(5)	2.226(17)	W-C(6)	2.209(5)
W-N	2.206(14)	W-O(3)	2.148(4)
C(1)-O(1)	1.152(18)	C(1)-O(1)	1.148(8)
C(2)-O(2)	1.141(23)	C(2)-O(2)	1.137(7)
C(3)-N	1.075(23)	C(3)-C(4)	1.506(9)
C(3)-O(3)	1.267(24)	C(3)-O(3)	1.252(8)
		C(3)-O(4)	1.177(8)
		C(4)-F(1)	1.230(9)
		C(4)-F(2)	1.248(12)
		C(4)-F(3)	1.181(10)
C(4)-C(5)	1.34(3)	C(5)-C(6)	1.388(8)
C(5)-C(6)	1.33(3)	C(6)-C(7)	1.316(7)
C(6)-C(7)	1.51(2)	C(7)-C(8)	1.547(7)
C(7)-C(8)	1.54(2)	C(8)-C(9)	1.540(7)
C(7)-C(14)	1.56(2)	C(8)-C(15)	1.542(7)
C(7)-C(20)	1.55(2)	C(8)-C(21)	1.546(7)

Table 3. Selected Bond Angles (deg) for 3 and 4

complex 3		complex 4	
C(1)-W-C(2)	81.1(8)	C(1)-W-C(2)	78.8(3)
C(1)-W-N	148.6(7)	C(1)-W-O(3)	149.28(21)
C(2)-W-N	85.6(6)	C(2)-W-O(3)	88.54(19)
W-C(1)-O(1)	173.5(20)	W-C(1)-O(1)	175.3(6)
W-C(2)-O(2)	176.7(15)	W-C(2)-O(2)	172.3(5)
W-N-C(3)	170.1(12)	W-O(3)-C(3)	127.5(3)
C(4)-C(5)-C(6)	148.7(16)	C(5)-C(6)-C(7)	146.5(5)
C(5)-C(6)-C(7)	126.6(15)	C(6)-C(7)-C(8)	126.1(4)
N-C(3)-O(3)	178.5(20)	O(3)-C(3)-O(4)	128.7(6)
		C(4)-C(3)-O(3)	114.5(5)
		C(4)-C(3)-O(4)	116.8(6)

clopentadienyl plane, possibly because of the steric effect. In constrast, in the rhenium allene complex with a three leg piano stool structure, the C—C vector is tilted about 45° to the cyclopentadienyl plane.[22] The length of the coordinated C=C bond (1.34(3) Å) in **3** is only slightly longer than that of the uncoordinated one (1.329(25) Å). However, the length of the coordinated C=C bond (1.388(8) Å) in **4** is significantly longer than that of the uncoordinated C=C bond (1.316(7) Å). Namely, coordination of allene lengthens the coordinated C=C bond compared to that of the noncoordinated allene double bond. The W—CH_2 bond length is longer than the corresponding W—C(central) distance in both complexes, as observed in many metal π-allene complexes. The distance from the metal to the central carbon of an allene ligand is typically 0.05–0.19 Å shorter than the distance from the metal to the terminal carbon. This has been attributed to overlap between a filled d orbital on the metal and both of the unoccupied orthogonal π^* orbitals of the central carbon.[23] The allene ligand in **3** is bent in a fashion found in all η^2-allene complexes.[24] The crystal structures of 14 transition metal complexes of acyclic allenes have been previously reported.[25] These contain a total of 17 independent allene ligands and exhibit C=C=C angles that range from 134.5 to 160°, with an average of 150(7)°. The C=C=C angles of 149(1)° in **3**, and 149(1)° in **4**, are both close to the average.

For the isocyanato ligand in **3**, the W-N, N-C, and C-O distances are 2.16(1), 1.16(2), and 1.21(2) Å, respectively.

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These distances may be compared to the distances 1.993(6), 1.129(9), and 1.22(1) Å in the Mn compound *fac*-Mn$(CO)_3$(dppe)(NCO)[14] and to the distances 2.127(8), 1.12(1), and 1.24(2) Å in the Mo compound Cp(CO)Mo$(PPh_3)_2$(NCO).[26] The geometry of the tungsten–isocyanate fragment does not depart significantly from linearity, the W–N–C and N–C–O angles being 170(1) and 179(2)°. The NCO ligands in all three of these compounds are linear. Although it is difficult to distinguish M–NCO from M–OCN ligation by X-ray only, the fact that the N–C distance is much shorter than the C–O distance is consistent with the NCO sequence rather than the M–OCN arrangement. This problem has been addressed previously.[27]

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Supplementary Material Available: Details of the structural determination for complexes **3** and **4** including tables of crystal data, fractional coordinates, anisotropic thermal parameters, and complete bond distances and angles (13 pages). Ordering information is given on any current masthead page.

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