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Synthesis of Tungsten Complexes Containing an Intramolecularly Coordinated Alkyne Group

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Summary: Irradiation of cyclopentadienyltungsten carbonyl complexes bearing a pendant alkyne group promoted intramolecular displacement of CO by the alkyne. The resulting complexes, which contain an intramolecularly coordinated alkyne group, were characterized by ^1H and ^{13}C NMR spectroscopy.

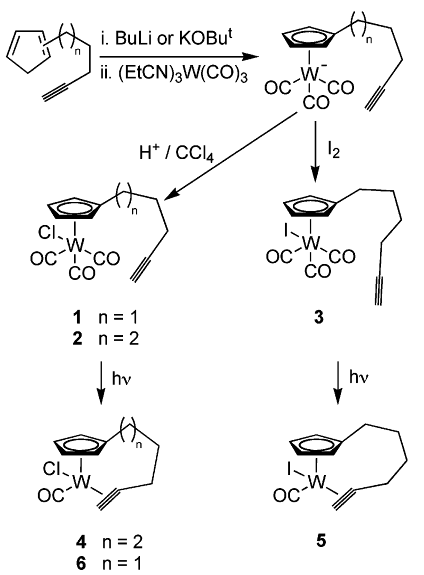
Introduction

We are interested in systems bearing pendant alkyne groups as potential precursors of organometallic cage compounds.[1−4] To date, there have been relatively few metal complexes that contain a facially coordinated ligand (e.g., cyclopentadienyls, arenes, triaza-macrocycles) and alkynes coordinated in an intramolecular manner. Krivykh et al.[5] reported chromium π-arene complexes containing intramolecularly coordinated alkyne groups, and previously we reported a tri(alkynyl)triazacyclononane complex of copper in which one of the alkyne units was bound to the metal center.[1]

Alkynes are particularly reactive, and their presence can complicate coordination of other binding groups. For example, Krivykh et al. synthesized their chromium alkyne complexes by attachment of an alkyne group to (hydroxymethylbenzene)chromium tricarbonyl via an ether linkage, rather than by formation of a chromium π-arene complex directly from an alkynylbenzene, presumably to prevent the alkyne from reacting with the metal precursor in the initial coordination step. In our studies of trialkynyltriazacyclohexane and trialkynyltriazacyclononane systems,[1−4] careful choices of conditions were required to form N_3-bound complexes, forcing conditions giving intractable polymeric materials. In only one of these cases were we able to detect and characterize a well-defined complex containing an intramolecularly cooordinated alkyne group.[2]

Gleiter and co-workers[6] reported the preparation of cyclopentadienylcobalt complexes bearing two pendant alkyne groups by reaction of the appropriate alkynylcyclopentadienide ion with a Co(I) source. Cyclodimerization of these pendant alkynes promoted by the metal center produced a doubly bridged cyclopentadienyl−cyclobutadienyl cobalt complex. There is a large body of work concerned with cyclopentadienyltungsten-alkyne compounds,[7−9] but none of these involve intramolecular coordination of pendant alkynes. In this paper we report the synthesis of cyclopentadienyltungsten complexes bearing a single pendant alkyne and subsequent coordination of the alkynyl group.

Scheme 1



Results and Discussion

The pent-4-ynylcyclopentadiene and hex-5-ynylcyclopentadiene were synthesized by reaction of the appropriate alkynyl iodides with sodium cyclopentadienide[10] and were purified by distillation. Deprotonation of the cyclopentadienes using a strong base (butyllithium or potassium *tert*-butoxide) and reaction of the resulting cyclopentadienides with tris(propionitrile)tungsten tricarbonyl gave the corresponding anionic cyclopentadienyltungsten tricarbonyl complexes (Scheme 1).[11] Other workers have synthesized cyclopentadienyltungsten compounds by direct reaction of tris(alkanenitrile)tungsten tricarbonyl with cyclopentadiene. With

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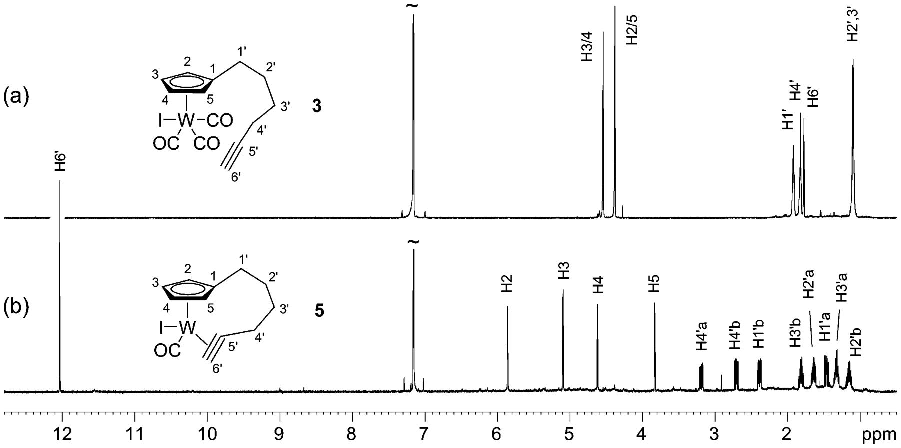

Figure 1. ^{1}H NMR spectra (500.13 MHz, benzene-d_6) of (a) a freshly prepared sample of **3** and (b) a sample of **5**, prepared by irradiation of a solution of **3** in a Pyrex NMR tube with a tungsten lamp at ambient temperature. The solvent signal is marked with a tilde (~).

the alkynycyclopentadiene systems this method yields only intractable materials, presumably because the alkyne is more reactive toward the tungsten source than the cyclopentadiene. The high reactivity of alkynes toward tungsten sources to form π-alkyne complexes is well known.[7,8,12–14]

Treatment of the anionic cyclopentadienyltungsten tricarbonyl complexes with acetic or dilute hydrochloric acid followed by CCl_4 gave the neutral chloride adducts **1** and **2**, while the neutral iodide adduct **3** was obtained by treatment of the corresponding anionic complex with I_2. The chlorides **1** and **2** were both solids and could be obtained analytically pure, but the iodide **3**—a viscous liquid—appeared to undergo slow polymerization when concentrated and could not be obtained in pure form.

The carbonyl stretches in the infrared spectrum of the iodide **3** occur at 2030 and 1946 cm^{-1}, while the chlorides **1** and **2** have stretches at ca. 2040 cm^{-1} and ca. 1950 cm^{-1}, similar to values for the parent compounds ($CpW(CO)_3X$).[15] Mass spectra (FAB) showed the major fragment for **1**, **2**, and **3** to be $[M - 3CO]^+$, with the expected isotopic patterns. High-resolution spectra of the molecular ions for **1** and **3** could be obtained, but in the case of **2** extensive fragmentation occurred and no molecular ion could be detected.

The ^{1}H NMR spectra of **1**, **2**, and **3** are all similar, as are the ^{13}C NMR spectra, the only differences being due to the additional $-CH_2-$ found in **2** and **3**. The ^{1}H NMR spectrum of the iodide **3** (Figure 1a) shows two signals for the cyclopentadienyl protons, one signal for the terminal alkyne proton at δ 1.7 (t, $J = 2.7$ Hz), and three signals (H2′ and H3′ overlapping) for the chain protons. The ^{13}C NMR spectrum of **3** contains two carbonyl signals (approximate intensity ratio 2:1, as expected for a four-legged piano stool arrangement in which two are cis and one is trans to the halide) and two signals for the alkyne carbons at δ 84 and 69.

Upon irradiation of dilute benzene-d_6 (for NMR studies) or THF (for IR studies) solutions of the hexynyl compound **2** or **3** with visible light (tungsten lamp, Pyrex vessel), the color changed from red to green. Products assigned as **4** and **5** were formed (Scheme 1), by intramolecular displacement of CO by the pendant alkyne group. These compounds could not be isolated, but were characterized spectroscopically. The infrared spectra of these products show a single carbonyl stretch at 1924 cm^{-1} (chloride, **4**) and 1934 cm^{-1} (iodide, **5**), suggesting that only one carbonyl is present;[8] related compounds with two C≡O groups, e.g., $CpW(CO)_2(PPh_3)I$,[16] give two stretches. FAB mass spectra of the compounds showed extensive fragmentation; the only peaks that could be assigned were due to $(M - Cl)$ in the case of **4**, which showed the expected isotopic pattern.

The differences between the ^{1}H and ^{13}C NMR spectra of **2** and **3** and their chelated analogues **4** and **5** are striking (spectra for **3** and **5** are compared in Figure 1). In the ^{1}H NMR spectra (e.g., Figure 1) the main difference is the shift in the position of the alkynyl proton upon coordination of the alkyne group, from δ 1.7 to ca. δ 12.0. The four-bond H4′–H6′ coupling constant is reduced from 2.7 Hz, to 1.0 Hz, which may reflect reduction in bond order of the C5′–C6′ bond upon coordination of the alkyne group, and indeed, bond lengthening in alkyne groups upon coordination has been reported previously.[1] The alkynyl protons for **4** and **5** show ^{183}W satellites of ca. 5.0 Hz, indicating that the alkynyl proton is relatively close (through bonds) to the metal center, consistent with tungsten–alkyne coordination. In closely related complexes, e.g., $C_5H_5W(CO)(CH_3)(HC{\equiv}CCH_3)$,[8] similar chemical shifts and couplings are observed for the alkyne proton(s). Significant downfield shift of alkyne protons upon coordination of the alkyne to a metal has also been observed in other systems[17,18] and is indicative of the alkyne behaving as a four-electron donor.[9] The loss of carbonyls and coordination of the alkyne reduce the effective symmetry of the molecule, so that all nuclei in **4** and **5** are chemically nonequivalent. In the ^{1}H NMR spectrum of **5** (Figure 1b), the signals are well dispersed so that the spectrum

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is essentially first order, extensive coupling is evident, and all geminal, vicinal, and benzylic couplings were resolved.

In the ^{13}C NMR spectra of both **4** and **5**, only one carbonyl signal is observed, which corroborates the evidence from the infrared spectra, suggesting that the molecules contain only one carbonyl group. The signals due to the carbons of the coordinated alkyne are shifted downfield approximately 120 ppm to ca. δ 209 and ca. δ 185. In the ^{13}C NMR spectra of related complexes, e.g., $C_5H_5W(CO)(CH_3)(HC{\equiv}CCH_3)$,[8] similar chemical shifts are found for C≡O and C≡C carbons. The signal due to the CH_2 adjacent to the alkyne group in **4** and **5** also shifts significantly (ca. 18 ppm downfield) on coordination of the alkyne group.

In the displacement of CO by alkynes in **2** and **3**, intermolecular reactions are likely to compete with the intramolecular process. Close examination of the ^1H NMR spectra of solutions containing the products of intramolecular displacement (**4** and **5**) reveals numerous minor signals due to trace impurities (e.g., Figure 1b, δ 4−6.5, δ 11.5), which may be oligomeric byproducts arising from intermolecular displacement reactions. Irradiation of concentrated solutions of **2** and **3** led to reduced yields of **4** and **5** and formation of insoluble green-brown, presumably polymeric, materials. Attempts to isolate **4** and **5** by removal of solvent from clear solutions also resulted in formation of green-brown solids that could only partially be redissolved, suggesting that the intramolecular displacment products **4** and **5** themselves polymerize in concentrated mixtures.

In the case of the pentynyl complex **1**, the trimethylene chain tethering the alkyne group to the cyclopentadienyl ligand may be too short to accommodate the intramolecular displacement reaction readily. When even dilute solutions of the pentynyl complex **1** were irradiated, a mixture of unidentified products, along with significant quantities of a green-brown, presumably polymeric material, was formed. Among the numerous signals in the ^1H NMR spectrum of such samples, a signal at δ 11.92 (triplet with ^{183}W satellites, $J_{WH} = 5.1$ Hz, $J_{HH} = 1.1$ Hz) and signals at δ 5.71, 5.25, 5.21, and 3.01 are tentatively assigned to the alkynyl proton and the Cp protons of the complex **6** (Scheme 1). ^1H NMR signals consistent with the trimethylene chain of **6** occurred in the region δ 1−3.

Experimental Section

NMR spectra were recorded using a Bruker ARX 300 (300.13 MHz for ^1H, 75.45 MHz for ^{13}C), AV 500 (500.13 MHz for ^1H, 125.8 MHz for ^{13}C), or AV 600 (600.13 MHz for ^1H, 150.92 MHz for ^{13}C) and were referenced to solvent signals. Assignments of ^1H NMR and ^{13}C NMR spectra were made with the aid of HSQC, HMBC, and NOESY spectra. Mass spectra (FAB) were recorded using a VG Autospec mass spectrometer with a cesium ion source and a *m*-nitrobenzyl alcohol matrix. Microanalysis was performed by the Microanalytical Unit, Research School of Chemistry, Australian National University, Canberra. Tris(propionitrile)tungsten tricarbonyl[19] was prepared using a literature method.

(η^5-$C_5H_4CH_2CH_2CH_2CH_2C{\equiv}CH$)W(CO)$_3$I (3). A solution of hex-5-ynylcyclopentadiene (0.11 g, 0.75 mmol) and potassium *tert*-butoxide (72 mg, 0.64 mmol) in DMF (3 mL) was stirred for 30 min. A solution of tris(propionitrile)tungsten tricarbonyl (0.16 g, 0.37 mmol) in DMF (2 mL) was added, and the solution was stirred for 2 h. Then iodine (0.17 g, 0.66 mmol) was added, and the solution was stirred for 30 min. The solution was poured into water (10 mL) and extracted with chloroform (3 × 5 mL). The combined chloroform extracts were washed with 5% NaI solution (2 × 5 mL) and 10% $Na_2S_2O_3$ (2 × 3 mL) and dried ($MgSO_4$). The solvent was evaporated, and the residue was purified by chromatography on silica (20% $CHCl_3$/hexanes) to give **3** as a red liquid (70 mg, 35%). HR-MS (FAB): *m/z* 541.9476 ($C_{14}H_{13}IO_3{}^{186}W$ requires 541.9453). LR-MS (FAB): *m/z* 454, 455, 456, 458 (matches M − 3CO, $C_{14}H_{13}I^{182,183,184,186}W$). IR (THF): ν(CO) 2030, 1946 cm^{-1}. ^1H NMR (500.13 MHz, C_6D_6): δ 4.54 (apparent t, splitting 2.2 Hz, 2H, H2/5), 4.38 (apparent t, splitting 2.2 Hz, 2H, H3/4), 1.92 (apparent t, splitting 7.3 Hz, 2H, H1′), 1.82 (m, 2H, H4′), 1.70 (t, $J_{6',4'} = 2.7$ Hz, 1H, H6′), 1.05−1.15 (m, 4H, H2′ and H3′). ^{13}C NMR (125.8 MHz, C_6D_6): δ 226.28 (CO), 211.09 (2 × CO), 116.26 (C1), 92.89 (C2/C5), 89.44 (C3/C4), 83.69 (C5′), 69.35 (C6′), 30.41, 27.90 (C2′, C3′), 28.52 (C1′), 18.29 (C4′).

(η^5:η^2-$C_5H_4CH_2CH_2CH_2CH_2C{\equiv}CH$)W(CO)I (5). A solution of **3** in d_6-benzene in a Pyrex NMR tube cooled in a water bath (ca. 25 °C) was irradiated using a 150 W tungsten lamp. Reaction progress was monitored by ^1H NMR spectroscopy, and consumption of **3** was complete after 60 min. Yield: 59% by ^1H NMR. IR (THF): ν(CO) 1934 cm^{-1}. ^1H NMR (500.13 MHz, C_6D_6): δ 12.03 (t (with W satellites), $J_{6',4'} = 1.0$ Hz, $J_{W-H} = 5.0$ Hz, 1H, H6′), 5.86 (ddddd, $J_{2,3} = 3.1$ Hz, $J_{2,5} = 1.9$ Hz, $J_{2,4} = 1.8$ Hz, $J_{2,1'a} = 0.6$ Hz, $J_{2,1'b} = 0.5$ Hz, 1H, H2), 5.10 (dddd, $J_{3,4} = 3.3$ Hz, $J_{3,2} = 3.1$ Hz, $J_{3,5} = 2.0$ Hz, $J_{3,1'a} = 0.35$ Hz, 1H, H3), 4.62 (ddd, $J_{4,3} = 3.3$ Hz, $J_{4,5} = 2.8$ Hz, $J_{4,2} = 1.8$ Hz, 1H, H4), 3.83 (ddddd, $J_{5,4} = 2.8$ Hz, $J_{5,3} = 2.0$ Hz, $J_{5,2} = 1.9$ Hz, $J_{5,1'b} = 0.6$ Hz, $J_{5,1'a} = 0.4$ Hz, 1H, H5), 3.26 (dddddd, $J_{4'a,4'b} = 16.7$ Hz, $J_{4'a,3'a} = 7.7$ Hz, $J_{4'a,3'b} = 2.5$ Hz, $J_{4'a,6'} = 1.0$ Hz, $J_{4'a,2'a} = 0.5$ Hz, $J_{4'a,2'b} = 0.25$ Hz, 1H, H4′a), 2.70 (dddd, $J_{4'b,4'a} = 16.7$ Hz, $J_{4'b,3'b} = 10.4$ Hz, $J_{4'b,3'a} = 2.3$ Hz, $J_{4'b,6'} = 1.0$ Hz, 1H, H4′b), 2.39 (ddddd, $J_{1'b,1'a} = 16.5$ Hz, $J_{1'b,2'b} = 7.5$ Hz, $J_{1'b,2'a} = 3.0$ Hz. $J_{1'b,5} = 0.6$ Hz, $J_{1'b,2} = 0.5$ Hz, 1H, H1′b), 1.88 (ddddd, $J_{3'b,3'a} = 14.4$ Hz, $J_{3'b,4'b} = 10.4$ Hz, $J_{3'b,2'b} = 10.1$ Hz, $J_{3'b,2'a} = 3.7$ Hz, $J_{3'b,4'a} = 2.5$ Hz, 1H, H3′b), 1.64 (dddddd, $J_{2'a,2'b} = 14.8$ Hz, $J_{2'a,1'a} = 10.8$ Hz, $J_{2'a,3'a} = 6.6$ Hz, $J_{2'a,3'b} = 3.7$ Hz, $J_{2'a,1'b} = 3.0$ Hz, $J_{2'a,4'a} = 0.5$ Hz, 1H, H2′a), 1.55 (dddddd, $J_{1'a,1'b} = 16.5$ Hz, $J_{1'a,2'a} = 10.8$ Hz, $J_{1'a,2'b} = 2.9$ Hz, $J_{1'a,2} = 0.6$ Hz, $J_{1'a,5} = 0.4$ Hz, $J_{1'a,3} = 0.35$ Hz, 1H, H1′a), 1.32 (ddddd, $J_{3'a,3'b} = 14.4$ Hz, $J_{3'a,4'a} = 7.7$ Hz, $J_{3'a,2'a} = 6.6$ Hz, $J_{3'a,2'b} = 4.0$ Hz, $J_{3'a,4'b} = 2.3$ Hz, 1H, H3′a), 1.15 (dddddd, $J_{2'b,2'a} = 14.8$ Hz, $J_{2'b,3'b} = 10.1$ Hz, $J_{2'b,1'b} = 7.5$ Hz, $J_{2'b,3'a} = 4.0$ Hz, $J_{2'b,1'a} = 2.9$ Hz, $J_{2'b,4'a} = 0.25$ Hz, 1H, H2′b). ^{13}C NMR (150.9 MHz, C_6D_6): δ 228.14 (CO), 208.95 (C5′), 184.90 (C6′), 112.86 (C1), 104.96 (C3), 101.42 (C2), 84.46 (C4), 82.43 (C5), 36.23 (C4′), 27.28 (C1′), 26.32 (C3′), 25.42 (C2′).

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Supporting Information Available: Complete details for synthesis and characterization of pent-4-ynylcyclopentadiene, hex-5-ynylcyclopentadiene, and tungsten complexes **1**, **2**, **4**, and **6**. The materials are available free of charge via the Internet at http://pubs.acs.org.

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