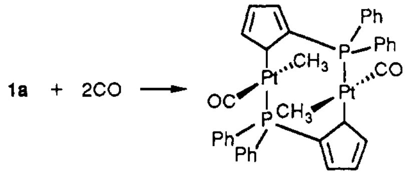
Organometallics **1990,** *9,* 289-291

center of symmetry, however, in contrast to the related complex $[Rh_2(CO)_2(\mu\text{-}\eta^5\text{-}C_5H_4PPh_2)_2]$.[6] If the two Pt atoms, the two P atoms, and the centroids of the two cyclopentadienyl rings are considered to form a six-membered ring, the molecule may be said to adopt a distorted-boat conformation. The distortion is such that the two P-Pt-Ph angles differ by 10°, for example. This unsymmetrical structure persists in solution at low temperature for both **1a** and **1b**, as evidenced by multinuclear magnetic resonance measurements (Table I). Thus, for example, the $^{31}P\{^1H\}$ NMR spectrum of **1a** at -55 °C consists of two doublets, each exhibiting both short- and long-range coupling to ^{195}Pt. Warming to 25 °C results in broadening of these signals, followed by coalescence, and heating to 100 °C produces a single, very broad resonance; decomposition occurs above this temperature, so a fast-exchange limiting spectrum is not obtained. Similar results are obtained for solutions of **1b**.

When a CH_2Cl_2 solution of **1a** is treated with carbon monoxide (1 atm) at ambient temperature, the 16-electron complex $[Pt_2Me_2(CO)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$ (**2a**) is obtained as a yellow solid in 90% yield (eq 2). Coordination of CO is accompanied by an η^5 to η^1 rearrangement of the cyclopentadienyl moiety,[9] and the face-to-face square-planar complex exists as that isomer in which the carbonyl and methyl groups lie mutually trans to one another.[10] This reaction is unusual in that an 18-electron complex gains a CO ligand but simultaneously becomes coordinatively unsaturated. In contrast to the case for **1a**, the NMR spectra of **2a** exhibit single methyl, carbonyl, and phosphorus resonances. The analogous reaction of **1b** produces an insoluble solid.[11]



(2)

Addition of 6-10 equiv of CNBu^t to a CH_2Cl_2 solution of **1a** or **1b** results in cleavage of the Pt-Cp linkages and generation of a monomeric complex of the form *trans*-$[PtR(CNBu^t)_2(Ph_2PC_5H_4)]$ (**3a**, R = Me; **3b**, R = Ph).[12] The $^{31}P\{^1H\}$ NMR spectra of **3a** and **3b** exhibit $^1J_{PtP}$ values around 1500 Hz, consistent with the P atom lying trans to R,[13] and the ^1H and $^{13}C\{^1H\}$ NMR spectra exhibit only two and three signals, respectively, for the C_5H_4 group, which suggests that the cyclopentadienyl group is uncoordinated. We formulate the complexes as zwitterions, having a formal positive charge on platinum and a negative charge associated with the cyclopentadienyl ring. Complex **3a** and the isonitrile analogue of **2a**, namely $[Pt_2Me_2(CNBu^t)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$, are in dynamic equilibrium in solution, **2a** being favored in the absence of excess isonitrile. Thus, when a benzene solution of **1a** is treated with 2 mol equiv of CNBu^t (1 mol equiv per Pt) $[Pt_2Me_2(CNBu^t)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$ is formed in near-quantitative yield, as evidenced by NMR spectroscopy.[14]

Complexes 1 and 2 represent suitable substrates for studying dinuclear elimination reactions from complexes in which the organic fragments are constrained in one molecule but are attached to different metal centers, and these and related reactions will be discussed elsewhere.

Acknowledgment. Financial support from the University of Missouri—St. Louis is gratefully acknowledged. M.L. thanks Mallinckrodt Inc. for a graduate fellowship.

Supplementary Material Available: $^{31}P\{^1H\}$ NMR spectrum of **1a** in $CDCl_3$ solution at -55 °C and tables of crystal data, data collection, and solution and refinement parameters, atomic coordinates, bond distances and angles, anisotropic displacement coefficients, and hydrogen atom coordinates (10 pages); a table of observed and calculated structure factors (31 pages). Ordering information is given on any current masthead page.

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(9) O'Connor, J. M.; Casey, C. P. *Chem. Rev.* **1987**, *87*, 307-318.

(10) NMR data (δ) for **2a**·$0.6CH_2Cl_2$ in $CDCl_3$ solution: ^1H NMR CH_3 0.65 (d, $^3J_{PH}$ = 7 Hz, $^2J_{PtH}$ = 63 Hz), C_5H_4 4.90 (d, $^3J_{PH}$ = 13 Hz, $^2J_{PtH}$ = 148 Hz), 6.28 (m), 6.60 (m), and 7.40 (m), CH_2Cl_2 5.32 (0.6 molecules per dimer by integration); $^{13}C\{^1H\}$ NMR CH_3 4.0 (d, $^2J_{PC}$ = 7 Hz, $^1J_{PtC}$ = 564 Hz), C_5H_4 60.5 (dd, $^2J_{PC}$ = 57 Hz, 22 Hz), 120.5 (d, J_{PC} = 13 Hz), 134.4 (d, J_{PC} = 10 Hz), and 145.2 (d, J_{PC} = 12 Hz), C attached to P not observed, CO 180.3 (d, $^2J_{PC}$ = 6 Hz, $^1J_{PtC}$ = 1103 Hz); $^{31}P\{^1H\}$ NMR 12.5 ($^1J_{PtP}$ = 2659 Hz). Anal. Calcd for $C_{38.6}H_{35.2}Cl_{1.2}O_2P_2Pt_2$: C, 45.20; H, 3.46. Found: C, 45.01; H, 3.56. IR (ν(CO), KBr pellet): 2050 cm^{-1}.

(11) The IR spectrum of this solid exhibits a band at 2056 cm^{-1} due to ν(CO). The compound may be the phenyl analogue of **2a** or an oligomeric form.

(12) Selected NMR data (δ, $CDCl_3$ solution) for **3a**: ^1H NMR CH_3 0.65 (d, $^3J_{PH}$ = 6 Hz, $^2J_{PtH}$ = 58 Hz), $C(CH_3)_3$ 1.10 (s), C_5H_4 6.32 (s) and 6.34 (s); $^{13}C\{^1H\}$ NMR CH_3 -12.5 (d, $^2J_{PC}$ = 70 Hz, $^1J_{PtC}$ = 391 Hz), $C(CH_3)_3$ 29.5 (s), $C(CH_3)_3$ 58.2 (s), C_5H_4 92.3 (d, J_{PC} = 74 Hz), 110.0 (d, J_{PC} = 15 Hz), and 116.0 (d, J_{PC} = 17 Hz); $^{31}P\{^1H\}$ NMR 2.5 ($^1J_{PtP}$ = 1568 Hz). **3a** loses CNBu^t on attempted isolation and so has not been obtained as an analytically pure material. Selected NMR data (δ, $CDCl_3$ solution) for **3b**: ^1H NMR $C(CH_3)_3$ 1.10 (s), C_5H_4 6.40 (m) and 6.47 (m); $^{13}C\{^1H\}$ NMR $C(CH_3)_3$ 29.1 (s), $C(CH_3)_3$ 58.4 (s), C_5H_4 90.5 (d, J_{PC} = 74 Hz), 110.4 (d, J_{PC} = 16 Hz), and 116.3 (d, J_{PC} = 17 Hz); $^{31}P\{^1H\}$ NMR -2.1 ($^1J_{PtP}$ = 1484 Hz). Anal. Calcd for $C_{33}H_{37}N_2PPt$: C, 57.64; H, 5.38; N, 4.07. Found: C, 57.17; H, 5.38; N, 4.40.

(13) Anderson, G. K.; Clark, H. C.; Davies, J. A. *Inorg. Chem.* **1981**, *20*, 3607-3611.

(14) Selected NMR data (δ) for $[Pt_2Me_2(CNBu^t)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$ ($CDCl_3$ solution): ^1H NMR CH_3 0.50 (d, $^3J_{PH}$ = 6 Hz, $^2J_{PtH}$ = 62 Hz), $C(CH_3)_3$ 0.88 (s), C_5H_4 5.18 (d, $^3J_{PH}$ = 12 Hz, $^2J_{PtH}$ = 141 Hz), 6.22 (m), and 6.40 (m) (remaining signal obscured); $^{13}C\{^1H\}$ NMR CH_3 -1.0 (d, $^2J_{PC}$ = 7 Hz, $^1J_{PtC}$ = 541 Hz), $C(CH_3)_3$ 29.6 (s, $^3J_{PtC}$ = 32 Hz), $C(CH_3)_3$ 54.6 (s, $^1J_{PtC}$ not observed); $^{31}P\{^1H\}$ NMR 12.6 ($^1J_{PtP}$ = 3028 Hz).

Preparation and Chemical Reactivities of the Tungsten Allenyl Complex $CpW(CO)_3CH{=}C{=}CH_2$

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Summary: The tungsten propargyl complex $CpW(CO)_3CH_2C{\equiv}CH$ (**1**; Cp = η^5 C_5H_5) readily converts to the η^1-allenyl complex $CpW(CO)_3CH{=}C{=}CH_2$ (**2**) when dissolved in benzene or heated in CH_3CN. A rough estimation of the energy of activation for such a process possibly indicates 1,3-tungsten sigmatropic rearrangement. The reaction of tetracyanoethylene with **1** or **2** occurs readily in both cases to give the complex $CpW(CO)_3C_5H_3(CN)_4$ (**3**) with a cyclopentene ring bonded to W in a η^1 fashion. At 70 °C, complex **2** reacts with $Fe_2(CO)_8(\mu\text{-}CH_2)$ to produce a tungsten-substituted trimethylenemethane iron carbonyl complex, $CpW(CO)_3(\mu\text{-}\eta^4\text{-}C_4H_5)Fe(CO)_3$ (**4**). The structure assignment of complex **4** is based on spectroscopic data.

The chemistry of organometallic complexes containing one or more M-C σ bonds has long been a subject of interest.[1] However, due to its rarity, chemical reactivities

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(1) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 94, and references therein.

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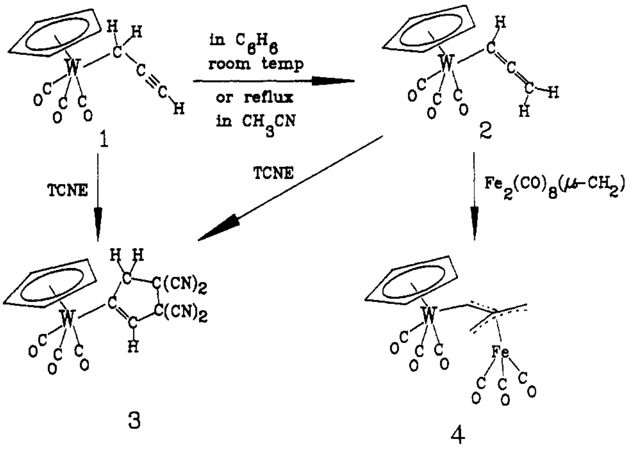
of the transition-metal η^1-allenyl complexes are less known. The iron allenyl complex[2] $CpFe(CO)_2(\eta^1\text{-}\sigma\text{-}CH{=}C{=}CH_2)$ was first thought to be a propargyl complex with a η^1-σ-$CH_2C{\equiv}CH$ ligand. It was later pointed out that the relatively large coupling constant between the methylene and methyne protons could only be derived from the allenyl π-interaction.[3] Recently, Seyferth[4] reported that the reaction of propargyl bromide with diiron anion yields products by which one can infer the presence of an allenyl ligand. In this communication, we report the isolation of a tungsten propargyl complex, its transformation to the corresponding allenyl complex, and the chemical reactivities of the latter compound.

The reaction of the tungsten anion $CpW(CO)_3^-$ with propargyl bromide at room temperature gave the bright yellow complex $CpW(CO)_3CH_2C{\equiv}CH$ (**1**)[5] as the major product (yield 76%). The $C{\equiv}C$ stretching of **1** appeared as a weak absorption peak at 2088 cm^{-1} in the IR spectrum.[6] In the ^1H NMR spectrum, a small coupling constant of 2.8 Hz was observed for the four-bond coupling ^4J of the methylene and methyne protons. In the ^{13}C NMR spectrum, the peak attributed to the methylene group was observed in the upfield (−33.3 ppm) region. Complex **1** in the solid state is unstable, even at low temperature, but is stable in CH_3CN solution. When dissolved in C_6D_6, complex **1** readily undergoes tautomerization to form $CpW(CO)_3(\eta^1\text{-}CH{=}C{=}CH_2)$ (**2**)[7] in a 100% NMR yield (91% isolated yield). Complex **2** could also be prepared from the thermolysis of **1** in acetonitrile. A much broader absorption peak at 1926 cm^{-1} was observed in the IR spectrum, most likely due to the overlapping of the characteristic absorption of the allenyl group[3,6a] with that of ν_{CO}. In the ^1H NMR spectrum, particularly diagnostic is a relatively large ^4J coupling between the methylene and methyne protons (6.7 Hz). This is very similar (6.5 Hz) to that observed previously for the iron compound $CpFe(CO)_2CH{=}C{=}CH_2$.[2] Both protons show a coupling to the W atom with coupling constants, J_{WH}, of 4.3 (α) and 2.7 (γ) Hz. In the ^{13}C NMR spectrum, the peak attributed to the methylene group was observed in the downfield (48.6 ppm) region. Unlike the ^1H NMR system, only the α-carbon is coupled to the W atom with a coupling constant of 47 Hz. It is interesting that while the two parent molecular ion peaks are both absent, the mass spectra of **1** and **2** show distinctly different fragmentation patterns. The primary cleavage for **2** occurs at the M–CO bond, whereas for **1**, it occurs at the M–propargyl bond. No $(M - CO)^+$ fragment (m/z = 346, W = 186) could be detected for **1**, possibly indicating a stronger M–C(allenyl) bond relative to the M–C(propargyl) bond.[8]

Scheme I



Two possible pathways for the transformation of **1** to **2** are 1,3-hydrogen and 1,3-tungsten sigmatropic rearrangement.[9] On the basis of the ready transformation of **1** at room temperature in C_6D_6, it seems likely that **2** is formed by a 1,3-tungsten sigmatropic rearrangement of **1**. This hypothesis was supported by the NMR monitoring of formation of **2**. Kinetic studies of the isomerization were carried out by ^1H NMR spectroscopy in $CDCl_3$ solution. A very rough estimate[10] of the value of energy of activation is in the range of 19 (C_6D_6) to 23 ($CDCl_3$) kcal/mol. The 1,3-hydrogen shift in propene has been found by ab initio calculations to proceed via an *antarafacial* transition state, whose energy is close to 93 kcal/mol.[11] For many substituted-propargyl–metal complexes, no such transformation has been observed. This is probably due to steric effects.

Treatment of **1** with tetracyanoethylene (TCNE) at room temperature for 15 min gave, in greater than 95% isolated yield, the air-stable adduct **3** as yellow crystals. A reaction of **2** with TCNE was similarly carried out in benzene and gave the spectroscopically identical product with slightly less yield (80% isolated). Such metal-assisted [3 + 2] cyclization[12] has been previously observed for

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(2) Jolly, P. W.; Pettit, R. *J. Organomet. Chem.* **1968**, *12*, 491.

(3) (a) Johnson, M. D.; Mayle, C. *J. Chem. Soc. D.* **1969**, 192. Several π-allenyl systems are known: (b) Wojcicki, A. *Adv. Organomet. Chem.* **1974**, *12*, 31. (c) Lennon, P.; Madhavarao, M.; Rosan, A.; Rosenblum, M. *J. Organomet. Chem.* **1976**, *108*, 93. (d) Benaim, J.; Merour, J. Y.; Roustan, J. L. *Tetrahedron Lett.* **1971**, 983. (e) Casey, C. P.; Austin, E. A. *J. Am. Chem. Soc.* **1988**, *110*, 7106 and references therein.

(4) Seyferth, D.; Womock, G. B.; Ancher, M.; Dewan, J. C. *Organometallics* **1989**, *8*, 430.

(5) Spectroscopic data for **1**: IR (THF) 3298 (ν_{CH}), 2088 ($\nu_{C\equiv C}$), 2020 and 1920 (ν_{CO}) cm^{-1}; ^1H NMR (CD_3CN) δ 5.57, 2.18 (t, J_{HH} = 2.8 Hz, CH), 1.90 (d, CH_2, J_{HW} = 3.8 Hz); ^{13}C NMR (CD_3CN) δ 231.2 (J_{WC} = 130 Hz), 219.6 (J_{WC} = 159 Hz) (3 CO's), 94.3 (Cp), 92.0 ($-C{\equiv}$), 68.4 (CH), −33.3 (CH_2, J_{CW} = 30 Hz); mass spectrum m/e 335 ($M^+ - CH_2CCH$), 307 ($M^+ - CH_2CCH - CO$), 279 ($M^+ - CH_2CCH - 2CO$). Anal. Calcd for $C_{11}H_8O_3W$: C, 35.51; H, 2.17. Found: C, 35.78; H, 2.09.

(6) (a) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; Wiley: New York, 1980; p 209. (b) Thomasson, J. E.; Robinson, P. W.; Ross, D. A.; Wojcicki, A. *Inorg. Chem.* **1971**, *10*, 2130. (c) Jolly, P. W.; Pettit, R. *J. Organomet. Chem.* **1968**, *12*, 491. (d) King, R. B. *Inorg. Chem.* **1963**, *2*, 531.

(7) Spectroscopic data for **2**: IR (C_6H_6) 2023 (s) and 1926 (s, br) (ν_{CO}) cm^{-1}; ^1H NMR (C_6D_6) δ 5.47 (t, J_{HH} = 6.7 Hz, J_{WH} = 4.3 Hz, CH) 4.51 (s, Cp), 4.06 (d, J_{WH} = 2.7 Hz, CH_2); ^{13}C NMR (C_6D_6) δ 228.6 (J_{WC} = 128 Hz), 216.2 (J_{WC} = 154 Hz) (3 CO's), 209.1 (${=}C{=}$), 92.5 (Cp), 62.2 (CH_2), 48.6 (J_{WC} = 47 Hz, CH); mass spectrum m/e 346 ($M^+ - CO$), 318 ($M^+ - 2CO$), 290 ($M^+ - 3CO$). Anal. Calcd for $C_{11}H_8O_3W$: C, 35.51; H, 2.17. Found: C, 35.94; H, 2.29.

(8) (a) Heppert, J. A.; Thomas-Miller, M. E.; Scherubel, D. M.; Tagusagawa, F.; Morgenstern, M. A.; Shaker, M. R. *Organometallics* **1989**, *8*, 1199. (b) Casey, C. P.; Polichnowski, S. W.; Tuinstra, H. E.; Albin, L. D.; Calabrese, J. C. *Inorg. Chem.* **1978**, *17*, 3045. (c) Jolly, W. L. *Modern Inorganic Chemistry*; McGraw-Hill: New York, 1984; p 52. (d) Casey, C. P.; Brukhardt, T. J.; Bunell, C. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 2127.

(9) (a) Rutledge, T. F. *Acetylenes and Allenes*; Reinhold: New York, 1969; Chapter 1. (b) Overman, L. E.; Marlowe, K.; Clizbe, A. *Tetrahedron Lett.* **1976**, 599. (c) Spangler, C. W. *Chem. Ber.* **1979**, *76*, 187.

(10) The corresponding rate constants for the isomerization of **1** are 3.67×10^{-3}, 4.96×10^{-3}, and 6.62×10^{-3} min^{-1} at 310, 317, and 324 K, respectively. However, careful examination of the NMR tube revealed the decomposition of **1** to an unidentified solid, not detected by NMR spectroscopy, at temperatures above 310 K. The energy of activation was, therefore, estimated roughly from $E_a^+ = -RT \ln (0.693/(At_{1/2}))$, assuming $A = 10^{11}$.

(11) (a) Clark, T. *J. Am. Chem. Soc.* **1987**, *109*, 6838. (b) Clark, T. *J. Am. Chem. Soc.* **1989**, *111*, 761. (c) Bourner, D. G.; Brammer, L.; Green, M.; Orpen, A. G.; Reeve, C.; Schaverien, C. J. *J. Chem. Soc., Chem. Commun.* **1985**, 1409. (d) Rodwell, W. R.; Bouma, W. J.; Radom, L. *Int. J. Quantum Chem.* **1980**, *18*, 107. (e) Bernardi, F.; Robb, M. A.; Schelgel, H. B.; Tonachini, G. *J. Am. Chem. Soc.* **1984**, *106*, 1198.

(12) (a) Rosenblum, M.; Giering, W. P. *J. Am. Chem. Soc.* **1971**, *93*, 5299. (b) Raghu, S.; Rosenblum, M. *J. Am. Chem. Soc.* **1973**, *95*, 3060. (c) Rosenblum, M. *Acc. Chem. Res.* **1974**, *7*, 122. (d) Cutler, A.; Ehntholt, D.; Giering, W. P.; Lennon, P.; Raghu, S.; Rosan, A.; Rosenblum, M.; Tancrede, J.; Wells, D. *J. Am. Chem. Soc.* **1976**, *98*, 3495.

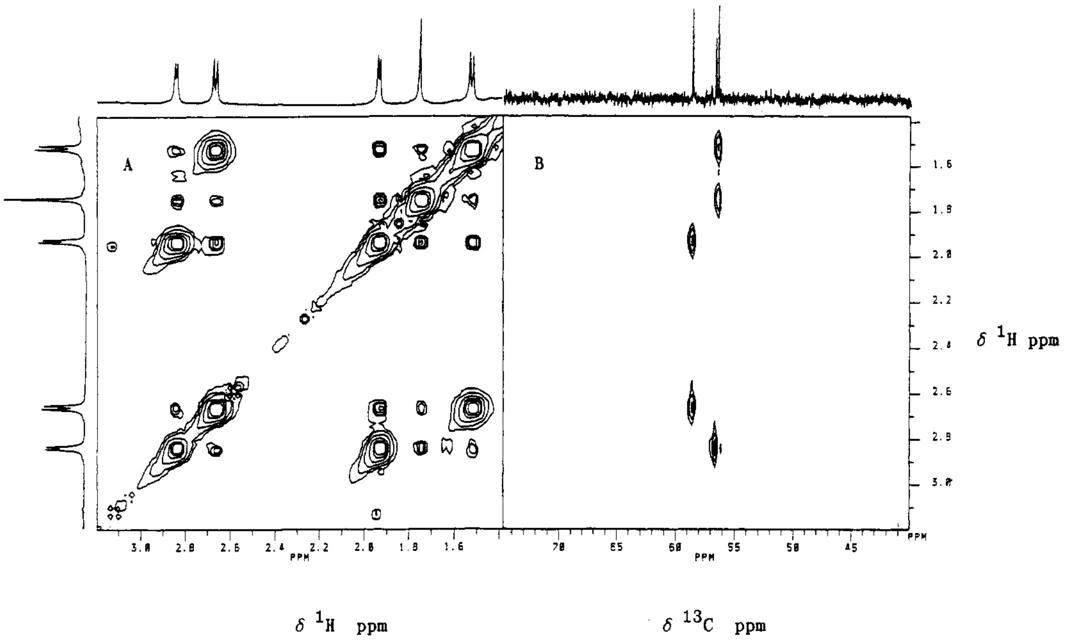

Figure 1. Contour plot of the ^1H–^1H long-range COSY (A) and ^1H–^{13}C correlation (B) spectra of complex 4. In A, all of the cross peaks, with the exception of those at (2.84, 1.93) and (2.66, 1.53), are due to coupled protons with coupling constants smaller than 0.7 Hz (not obvious from the 1D spectra). By a comparison of A and B, it is clear that mutually coupled proton pairs at 1.53, 2.66 and 1.93, 2.84 ppm are due to W coupling.

$CpFe(CO)_2(CH{=}C{=}CH_2)$. The spectroscopic data[13] for 3 suggest that the crystalline product is $CpW(CO)_3C_5H_3(CN)_4$. The ^1H NMR spectrum for 3 contains the expected singlet C_5H_5 resonance and 2:1 doublet/triplet resonances; the observed coupling constant of 1.5 Hz is typical of ^4J couplig of allylic type. The ^{13}C NMR signal at δ 147.1 is assigned to the α-carbon on the basis of ^{183}W satellites (J_{WC} = 63 Hz). Compared with the spectroscopic data of 1 and 2, the chemical shift is relatively downfield and the coupling constant J_{WC} is slightly larger. A single-crystal X-ray diffraction analysis of 3 provided an unambiguous structural assignment and will be reported separately.

The addition of 2 to a solution of the methylene-bridged iron complex $Fe_2(CO)_8(\mu\text{-}CH_2)$[14] results in the formation of the tungsten-substituted trimethylenemethane iron complex $CpW(CO)_3(\mu\text{-}\eta^4\text{-}C_4H_5)Fe(CO)_3$ (4)[15] at 70 °C (see Scheme I). Complex 1 reacts with $Fe_2(CO)_8(\mu\text{-}CH_2)$ in a similar fashion, since at this temperature, complex 1 readily converts to 2. The presence of the substituted trimethylenemethane ligand in 4 is indicated by the NMR data and FAB mass spectrum discussed below. Other researchers have observed similar formation of the trimethylenemethane ligand upon the reaction of allene with $Fe_2(CO)_8(\mu\text{-}CH_2)$.[14] To our knowledge this is the first reported instance of an iron complex with a metal-substituted trimethylenemethane ligand. The NMR spectroscopic data for 4 are sufficiently similar to those for many substituted trimethylenemethane ligands[16] so as to imply a similar structure. Complex 4 shows two sets of ^1H NMR doublets in the δ 1.5–2.9 spectral region due to a W coupling (coupling constant 1–3 Hz). The room-temperature ^{13}C NMR spectrum indicates that only three CO's, possibly on Fe, of 4 are fluxional. At −20 °C, the C atoms of the CO ligands of 4 appear as six signals with equal intensities. The assignments in the ^1H NMR spectra and the connection between $^{13}C\{^1H\}$ and ^1H NMR spectra are confirmed by the 2D NMR[17] spectra as shown in Figure 1. The FAB mass spectrum of 4 shows an envelope of parent molecular ion peaks, the distribution of which is in good agreement with the natural abundance of tungsten isotopes.

Further reactivities of these metal propargyl and allenyl complexes are currently under investigation.

Acknowledgment. This research has been supported by the National Science Council (NSC) of the Republic of China. The NMR instruments used were funded by the NSC Instrumentation Program. We thank reviewers for helpful comments and Peter Schwabland for reading the text.

Registry No. 1, 54761-81-8; 2, 123880-91-1; 3, 123880-92-2; 4, 123902-62-5; TCNE, 670-54-2; $CpW(CO)_3^-$, 12126-17-9; $Fe_2(CO)_8(\mu\text{-}CH_2)$, 73448-09-6; propargyl bromide, 106-96-7.

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(13) Spectroscopic data for 3: IR (KBr) 2255 (ν_{CN}), 2029, 1962, and 1909 (ν_{CO}) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 6.02 (s, 5 H, Cp), 5.92 (t, J_{HH} = 1.5 Hz, =CH), 3.86 (d, CH_2, J_{HH} = 1.5 Hz); ^{13}C NMR (CD_3COCD_3) δ 226.0 (J_{WC} = 122 Hz), 218.4 (J_{WC} = 147 Hz) (3 CO's), 147.1 (α-C, J_{WC} = 63 Hz), 128.5 (=CH), 113.0, 111.9 (4 CN's), 94.1 (Cp), 59.5 (–CH_2), 52.4, 46.8 (2 $C(CN)_2$'s); mass spectrum *m/e* 502 (M^+), 474 (M^+ − CO), 418 (M^+ − 3CO). Anal. Calcd for $C_{17}H_8N_4O_3W$: C, 40.80; H, 1.60; N, 11.20. Found: C, 40.87; H, 1.32; N, 11.34.

(14) (a) Sumner, C. E., Jr.; Collier, J. A.; Pettit, R. *Organometallics* **1982**, *1*, 1350. (b) Kao, S. C.; Lu, P. P. Y.; Pettit, R. *Organometallics* **1982**, *1*, 911. (c) Jones, M. D.; Kemmitt, R. D. W. *Adv. Organomet. Chem.* **1987**, *27*, 279. (d) Roustan, J.; Cadiot, P. *C. R. Seances Acad. Sci., Ser. C* **1968**, *268*, 734. (e) Seyferth, D.; Anderson, L. L.; Davise, W. M. *Organometallics* **1989**, *8*, 1371.

(15) Spectroscopic data for 4: IR (KBr) 2043, 2015, 1967, 1933, and 1910 (ν_{CO}) cm^{-1}; ^1H NMR (C_6D_6) δ 4.51 (s, 5 H, Cp), 2.84 (d, 1 H, J_{HH} = 3.1 Hz, =CH), 2.66 (d, 1 H, J_{HH} = 4.6 Hz), 1.93 (d, 1 H, J_{HH} = 3.1 Hz, =CH), 1.75 (s, 1 H, CH), 1.52 (d, 1 H, J_{HH} = 4.6 Hz); ^{13}C NMR (C_6D_6) δ 228.8, 219.0, 216.0 (3 CO's), 213.4 (br, 3 CO), 115.4 (=C=), 93.0 (Cp), 56.8 (J_{CW} = 59 Hz, –CH=), 58.7 (CH_2), 56.5 (CH_2); mass spectrum (FAB experiment was carried out on a JEOL JMSHX-110 mass spectrometer by the use of nitrobenzyl alcohol matrix) *m/z* 528 (M^+) and fragment ions corresponding to the consecutive loss of six CO's.

(16) Aumann, R.; Melchers, H. D.; Weidenhaupt, H. J. *Chem. Ber.* **1987**, *120*, 17.

(17) Homonuclear long-range COSY 2D spectra were recorded with the sequence 90°–t_1–τ–45°–t_2 (FID) at 300 K on a Bruker AM 300WB spectrometer, with 16 scans for each of the 128 t_1 values. The τ value was set to 0.16 s to emphasize coupling constants less than 0.7 Hz. Unshifted sine-bell filtering was used in both t_1 and t_2. Heteronuclear correlation spectra were recorded with use of the standard XHCORR pulse sequence at 300 K, with 128 scans for each of the 128 t_1 values. Sine-bell filtering, 90° shifted, was used in both t_1 and t_2. Both spectra are of the same data size (1K × 512) and are presented in the magnitude mode.