cently reported by the Lappert group.[11]

In preliminary attempts to isolate a true simple acyl of this system, we have found that reaction of **3** with HCl results in quantitative conversion to Cp_2ZrCl_2. Neither Ph_2PCH_3 nor any simple aldehyde is detected, and the fate of the bridging organic ligand is as yet undetermined. Further efforts along these lines are underway, as is a complete mechanistic study of the carbonylation process, which will be published separately.

Acknowledgment. We thank Mr. M. J. Knudsen for providing the 360-MHz NMR spectral data. Purchase of the NT-360 instrument was made possible by an instrumental grant from the National Science Foundation. Grateful acknowledgment is made to the Committee on Research of the University of California and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research. N.E.S. thanks the Camille and Henry Dreyfus Foundation for a Teacher–Scholar grant.

Registry No. 1, 74380-49-7; 2, 85369-34-2; 3, 91741-68-3; Ph_2PCH_3, 1486-28-8.

Supplementary Material Available: Experimental details of preparation and X-ray crystal structure determination of 3 and tables of atomic coordinates, bond lengths, bond angles, temperature factors, and derived hydrogen coordinates for 3 (6 pages). Ordering information is given on any current masthead page.

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[11] Bristow, G. S.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* 1982, 462.

Directed Synthesis of Phosphorus-Substituted Cyclopentadienones and Cyclobutadienes via Metal Carbonyl Promoted Coupling of Acetylenes Held Proximate to a Metal

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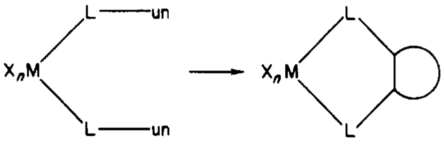
Summary: A strategy for the synthesis of heteroatom-substituted cyclobutadienes and cyclopentadienones via metal carbonyl promoted coupling of acetylenes held proximate via cis coordination to square-planar Pt(II) is outlined. Reaction of *cis*-$Cl_2Pt(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)_2$ with $Fe_2(CO)_9$ gives good yields of the η^4-cyclobutadiene complex $Cl_2Pt[(Ph_2P)_2C_4\text{-}t\text{-}Bu_2]Fe(CO)_3$ (II) which has been characterized by X-ray diffraction. Treatment of *cis*-$X_2Pt(Ph_2PC{\equiv}CR)_2$ (I, X = Cl, Br, I, Ph, 2-Me-C_6H_4, CF_3, C_6F_5; 2X = 1,2-$C_6H_4O_2$; R = Ph, Cy, $SiMe_3$) with $Fe_2(CO)_9$ generates cyclopentadienone derivatives IV (e.g., $Cl_2Pt[(Ph_2P)_2C_4Ph_2CO]Fe(CO)_3$) and/or V (e.g., $(C_6F_5)_2Pt[(Ph_2P)_2C_4Ph_2CO]$), examples of which have been characterized by X-ray analysis.

An attractive strategy for the synthesis of heteroatom-substituted carbocyclic systems is the directed coupling of two unsaturated groups held proximate *outside* the coordination sphere of a transition metal by cis coordination of the heteroatom substituents:



un = -C≡CR; C(H) = CRR'

In principle the method should be applicable to the generation of a wide variety of heteroatom-substituted ring systems including cyclobutadienes (un = C≡CR) or other products of acetylene cyclization and cyclobutanes (un = CH=CRR') via thermal, photochemical, or organometallic induced coupling.[1] Precoordination of the heteroatoms cis on a metal template has two advantages: (i) competitive involvement of the heteroatom in coupling mechanisms is avoided;[2] (ii) for steric reasons the unsaturated groups can be forced to approach one another quite closely thus facilitating coupling.[3,4] In this communication we describe the application of this strategy to the directed synthesis of novel ligated phosphorus-substituted cyclobutadienes and cyclopentadienones via reactions of the cis platinum(II) compounds $X_2Pt(Ph_2PC{\equiv}CR)_2$ (I, X = Cl, Br, I, Ph, 2-Me-C_6H_4, CF_3, C_6F_5; 2X = 1,2-$C_6H_4O_2$; R = Ph, *t*-Bu, Cy, $SiMe_3$) with $Fe_2(CO)_9$ and $(\eta^5\text{-}C_5H_5)Co(CO)_2$.

Reaction of I (X = Cl, R = *t*-Bu) (0.9 g, 1.13 mmol) with $Fe_2(CO)_9$ (0.41 g, 1.13 mmol) in dichloromethane at room temperature for 1 day followed by column chromatography (Florisil, eluant dichloromethane) and recrystallization from dichloromethane–petroleum ether (30–60 °C) afforded pale yellow crystals of II [76%; IR ($CHCl_3$) ν(CO) 2052, 1997, 1981 cm^{-1}, (Nujol) ν(Pt–Cl) 312, 290 cm^{-1}; ^{31}P NMR ($CDCl_3$) δ 40.3 (1:4:1 t, $^1J_{^{195}Pt-P}$ = 3760 Hz)]. X-ray crystallography[5] confirmed that II is an η^4-1,2-di-*tert*-butyl-3,4-bis(diphenylphosphino)cyclobutadiene complex (Figure 1). The corresponding photolytic reaction with $(\eta^5\text{-}C_5H_5)Co(CO)_2$ (C_6H_6, 6 h at room temperature) yielded the η^5-cyclopentadienyl η^4-cyclobutadiene complex III in 70% yield. The remarkable feature of these two reactions is the specificity for a single product, the cyclobutadiene complex in relatively high yield. The contrast with other (acetylene)iron carbonyl reactions[6] where cyclobutadiene complexes are produced in low yield, among a plethora of

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[1] For reviews of thermal, photochemical and metal catalyzed alkyne oligomerizations see: (a) Fuks, R.; Viehe, H. G. In "Chemistry of Acetylenes" Viehe, H. G., Ed.; Marcel Dekker: New York, 1969; Chapter 8. (b) Coyle, R. D. In "The Chemistry of the Carbon-Carbon Triple Bond"; Patai, S., Ed.; Wiley: New York, 1978; Chapter 12. (c) Collman, J. P.; Hegedus, L. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980; Chapter 13.

[2] Transition metal catalyzed or stoichiometric alkyne cyclizations are not generally applicable to N-, P-, or S-substituted acetylenes because the heteroatom, a Lewis base, competes effectively for metal coordination sites blocking the normal oligomerization mechanisms.

[3] Carty, A. J.; Taylor, N. J.; Johnson, D. K. *J. Am. Chem. Soc.* 1979, *101*, 5422.

[4] Carty, A. J.; Johnson, D. K.; Jacobson, S. E. *J. Am. Chem. Soc.* 1979, *101*, 5612.

[5] Crystal data for $PtFeCl_2P_2O_3C_{39}H_{38}\cdot 2CHCl_3\cdot 0.5CH_2Cl_2$: space group $P2_1/n$, a = 14.649 (1) Å, b = 18.517 (2) Å, c = 18.135 (2) Å, β = 91.52 (1)°, Z = 4, ρ_{calcd} = 1.647 g cm^{-3}, and $F(000)$ = 2404. The structure was solved and refined by using 4736 observed intensities measured on a Syntex $P2_1$ diffractometer to R and R_w values of 0.049 and 0.060, respectively. Full details of data collection, reduction, and refinement are listed in Table SI. The molecule consists of a planar cyclobutadiene ring with *cis*-di-*tert*-butyl and *cis*-diphenylphosphino groups, coordinated in η^4-fashion to an $Fe(CO)_3$ moiety and formed via coupling of the two phosphinoacetylene groups coordinated cis to the square-planar platinum atom. The C_4 ring is slightly rectangular with the C(4)–C(5) and C(6)–C(7) bond lengths (average 1.492 Å) being slightly longer than the C(5)–C(6) and C(4)–C(7) bonds (average 1.447 Å). The iron atom is symmetrically bound to the C_4 ring (Fe–C(4) = 1.989 (10) Å, Fe–C(5) = 2.109 (10) Å, Fe–C(6) = 2.136 (10) Å, and Fe–C(7) = 2.020 (10) Å).

[6] (a) Hubel, W. In "Organic Synthesis via Metal Carbonyls"; Wender, I., and Pino, P., Eds.; Wiley: New York, 1968; p 273. (b) Efraty, A. *Chem. Rev.* 1977, *77*, 691.

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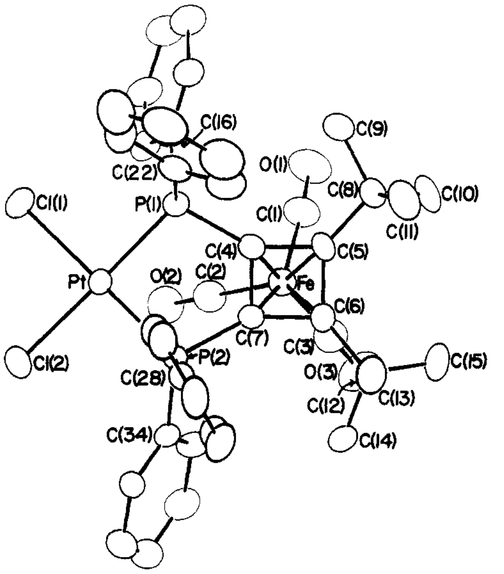

Figure 1. The molecular structure of $Cl_2Pt[(Ph_2P)_2C_4\text{-}t\text{-}Bu_2]\text{-}Fe(CO)_3 \cdot 2CHCl_3 \cdot 0.5CH_2Cl_2$ (II) as drawn by ORTEP. Solvent of crystallization is not shown.

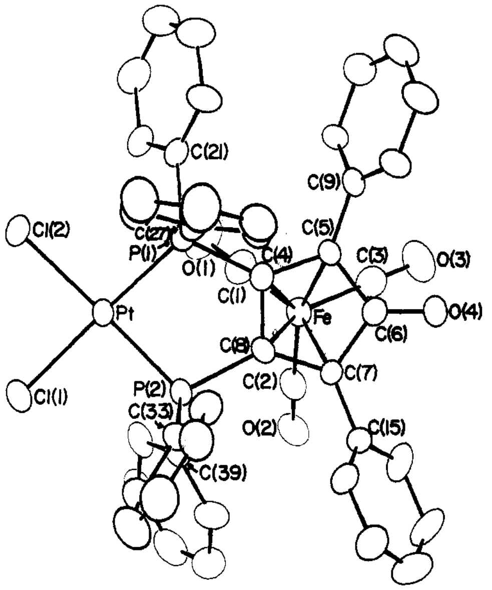

Figure 2. A perspective view of the structure of $Cl_2Pt\text{-}[(Ph_2P)_2C_4Ph_2CO]Fe(CO)_3 \cdot 3CHCl_3 \cdot 0.5C_6H_6$ (IV) drawn to illustrate the cyclopentadienone ring system. Solvent molecules are not shown.

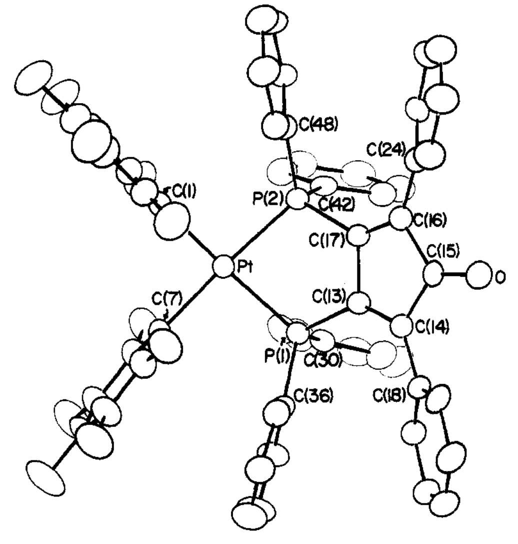

Figure 3. The structure of $(C_6F_5)_2Pt[(Ph_2P)_2C_4Ph_2CO] \cdot CHCl_3$ (V). Solvent is not included.

organometallic products, is particularly noteworthy. With I (X = Cl, R = Ph) and $Fe_2(CO)_9$ under identical conditions two major products brownish yellow IV (X = Cl, R = Ph) [47%; IR ($CHCl_3$) $\nu(CO)$ 2082, 2038, 2022, 1648 cm^{-1}, (Nujol) $\nu(Pt\text{–}Cl)$ 315, 295 cm^{-1}; ^{31}P NMR ($CDCl_3$) δ 40.2 (1:4:1 t, $^1J^{195}{}_{Pt\text{–}P}$ = 3611 Hz)] and brownish red V (X = Cl, R = Ph) [35%; IR (Nujol) $\nu(C{=}O)$ 1710 cm^{-1}, $\nu(Pt\text{–}Cl)$ 315, 292 cm^{-1}; ^{31}P NMR ($CDCl_3$) δ 27.0 (1:4:1 t, $^1J^{195}{}_{Pt\text{–}P}$ = 3532 Hz)] were isolated. The occurrence of a single ketonic $\nu(C{=}O)$ band in V and three additional terminal $\nu(CO)$ bands in IV suggested that IV might be related to V by coordination of an $Fe(CO)_3$ unit to the carbocycle of V. X-ray analysis[7] (Figure 2) revealed the presence of a bis(diphenylphosphino)diphenylcyclopentadienone ligand coordinated to an $Fe(CO)_3$ unit in IV. Thus V is the $PtCl_2$ derivative of the "free" phosphorus-substituted cyclopentadienone[8] (Figure 3). The preponderance of a single type of ring system, in this case a cyclopentadienone, from the coupling of the alkynes in I is again notable. Further evidence of the specificity of these coupling reactions was forthcoming from a more detailed investigation. Thus I (X = Br, I, Ph, 2-Me-C_6H_4, C_6F_5, 2X = 1,2-$C_6H_4O_2$, R = Ph; X = Cl, R = Cy) with $Fe_2(CO)_9$ gave in each case a mixture of the η^4-cyclopentadienone complex IV and the platinum complex of the bis(diphenylphosphino)cyclopentadienone V.[9] For I (X = CF_3, R = Ph) V was obtained free of the iron carbonyl complex, and for I (X = Cl, R = $SiMe_3$) the $Fe(CO)_3$ adduct IV was exclusively obtained. It is significant that all of the compounds of type V are deep red whereas the $Fe(CO)_3$ derivatives IV are pale to brownish yellow. We attribute this to a low-lying n → π^* transition in the "free" cyclopentadienone of V absent in the π-complexed species. There is an interesting contrast in structure between IV (X = Cl, R = Ph) and V (X = C_6F_5, R = Ph) in that the two phosphorus atoms of IV are syn with respect to the ring carbonyl atom C(6) whereas in the non-π-complexed dienone V the PPh_2 groups are anti to the corresponding atom C(15).[10] The

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(7) Crystal data for $PtFeP_2Cl_2O_4C_{44}H_{30} \cdot 3CHCl_3 \cdot 0.5C_6H_6$: space group $P2_1/c$, a = 23.609 (4) Å, b = 13.192 (3) Å, c = 18.845 (3) Å, β = 107.20 (2)°, Z = 4, ρ_{calcd} = 1.663 g cm^{-1}, $F(000)$ = 2756. Refinement of all non-hydrogen atoms with anisotropic thermal parameters using 4262 observed ($I \geq 3\sigma(I)$) data gave final R and R_w values of 0.047 and 0.055, respectively. Further details are given in Table SI.

(8) Crystal data for $PtP_2F_{10}OC_{53}H_{30} \cdot CHCl_3$: M_r = 1249.23 space group $P\bar{1}$, a = 12.106 (2) Å, b = 14.161 (3) Å, c = 16.377 (4) Å, α = 111.69 (2)°, β = 107.52 (2)°, γ = 92.05 (2)°, Z = 2, ρ_{calcd} = 1.691 g cm^{-3}, $F(000)$ = 1224. The structure was solved by the heavy-atom method using 5321 observed, counter measured reflections and refined to R and R_w values of 0.036 and 0.043, respectively.

(9) Satisfactory microanalyses have been obtained for all compounds synthesized. Selected spectroscopic and physical data are as follows. IV (X = Br, R = Ph): ≈20%; IR ($CHCl_3$) $\nu(CO)$ 2082, 2037, 2021, 1648 cm^{-1}, ^{31}P NMR ($CDCl_3$) δ 40.3 (1:4:1 t, $^1J^{195}{}_{Pt\text{–}P}$ = 3540 Hz). V (X = Br, R = Ph): ≈36%; IR (Nujol) $\nu(C{=}O)$ 1715 cm^{-1}; ^{31}P NMR ($CDCl_3$) δ 27.5 (1:4:1 t, $^1J^{195}{}_{Pt\text{–}P}$ = 3452 Hz). IV (X = 2-MeC_6H_4, R = Ph): 37%; IR ($CHCl_3$) $\nu(CO)$ 2075, 2028, 2017, 1638 cm^{-1}; ^{31}P NMR (C_6D_6) δ 44.3 and 48.2 (two 1:4:1 t, $^1J^{195}{}_{Pt\text{–}P}$ = 1814 Hz, $J_{P\text{–}P'}$ = 10 Hz). V (X = 2-MeC_6H_4, R = Ph): 6%; IR (Nujol) $\nu(C{=}O)$ 1710 cm^{-1}; ^{31}P NMR ($CDCl_3$) δ 29.5 (1:4:1 t, $^1J^{195}{}_{Pt\text{–}P}$ = 1659 Hz). IV (X = C_6F_5, R = Ph): 25%; IR ($CHCl_3$) $\nu(CO)$ 2080, 2033, 2023, 1643 cm^{-1}; ^{31}P NMR ($CDCl_3$) δ 38.5 (1:4:1 t, $^1J^{195}{}_{Pt\text{–}P}$ = 2374 Hz). V (X = C_6F_5, R = Ph): 25%; IR (Nujol) $\nu(C{=}O)$ 1718 cm^{-1}; ^{31}P NMR ($CDCl_3$) δ 26.0 (1:4:1 t, $^1J^{195}{}_{Pt\text{–}P}$ = 2185 Hz). V (X = CF_3, R = Ph): 19%; IR (Nujol) $\nu(C{=}O)$ 1712 cm^{-1}; ^{31}P NMR ($CDCl_3$) δ 29.7 (1:4:1 t, $^1J^{195}{}_{Pt\text{–}P}$ = 2018 Hz). IV (X = Cl, R = Cy): ~54%; IR ($CHCl_3$) $\nu(CO)$ 2077, 2028, 2021, 1631 cm^{-1}, (Nujol) $\nu(Pt\text{–}Cl)$ 324, 300 cm^{-1}; ^{31}P NMR ($CDCl_3$) δ 39.2 (1:4:1 t, $^1J^{195}{}_{Pt\text{–}P}$ = 3630 Hz). IV (X = Cl, R = $SiMe_3$): 32%; IR ($CHCl_3$) $\nu(CO)$ 2078, 2031, 2025, 1641 cm^{-1}, (Nujol) $\nu(Pt\text{–}Cl)$ 315, 291 cm^{-1}; ^{31}P NMR ($Me_2SO\text{-}d_6$) δ 43.4 (1:4:1 t, $^1J^{195}{}_{Pt\text{–}P}$ = 3556 Hz).

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syn stereochemistry with respect to the diene fragment presumably reduces steric interactions between bulky coordinated $Fe(CO)_3$ and $PtCl_2$ units.

An underlying reason for the facile and rather selective coupling of acetylenes observed here is that in complexes of type I the alkynes, when forced into close proximity by bulky groups in the coordination sphere of the platinum atom, exhibit intramolecular interactions.[3,11] It is possible that the nature of these intramolecular alkyne–alkyne contacts influences the direction of acetylene coupling since for R = Ph, Cy, and $SiMe_3$ coupling affords predominantly cyclopentadienones whereas for R = *t*-Bu, there is high specificity for cyclobutadiene synthesis. It is also significant to note that these metal carbonyl mediated cyclizations stand in sharp contrast to the corresponding thermal reactions where disubstituted naphthalenes are the principal products for R = Ph.[3] The overall ramifications of these observations for the synthesis of new substituted carbocycles and ligands are under investigation.

Registry No. I (X = Cl, R = *t*-Bu), 42847-18-7; I (X = Cl, R = Ph), 42847-16-5; I (X = Br, R = Ph), 71755-68-5; I (X = 2-MeC_6H_4, R = Ph), 91390-55-5; I (X = C_6F_5, R = Ph), 91409-33-5; I (X = CF_3, R = Ph), 91390-56-6; I (X = Cl, R = Cy), 91390-57-7; I (X = Cl, R = $SiMe_3$), 91390-58-8; II, 91390-50-0; III, 91390-48-6; IV (X = Br, R = Ph), 91390-41-9; IV (X = 2-MeC_6H_4, R = Ph), 91390-42-0; IV (X = C_6F_5, R = Ph), 91409-31-3; IV (X = Cl, R = Cy), 91390-44-2; IV (X = Cl, R = $SiMe_3$), 91390-45-3; IV (X = Cl, R = Ph), 91390-52-2; V (X = Cl, R = Cy), 91390-43-1; V (X = Br, R = Ph), 91390-46-4; V (X = 2-MeC_6H_4, R = Ph), 91390-47-5; V (X = C_6F_5, R = Ph), 91409-32-4; V (X = Cl, R = Ph) $Fe_2(CO)_9$, 91390-54-4; (η^5-C_5H_5)$Co(CO)_2$, 12078-25-0.

Supplementary Material Available: Details of collection, reduction, and refinement and tables of atomic coordinates, anisotropic thermal parameters, bond lengths and angles and structure factor amplitudes for all three compounds, II, IV, and V (102 pages). Ordering information is given on any current masthead page.

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(10) Comparison of the structures of IV (X = Cl, R = Ph) and V (X = C_6F_5, R = Ph) reveals that both molecules contain nonplanar C_5O ring systems. In IV the dihedral angle between the plane defined by the four diene carbon atoms C(4), C(5), C(7), and C(8) and the plane defined by C(5), C(7) and the carbonyl carbon C(6) is 16.9°. For V the same dihedral angle is only 5.1°. In IV the enone oxygen atom and the diene carbon atoms C(4) and C(8) have an anti stereochemistry with respect to the plane C(5), C(6), C(7) whereas in V, the corresponding diene carbon atoms C(13) and C(17) are syn to the carbonyl oxygen atom. The ketonic C=O bond length of 1.232 (14) Å in IV is arguably longer than in the non-π-complexed compound V (C(15)–O = 1.203 (9) Å).

(11) Forced intramolecular interactions in acetylenes frequently lead to unusual reactivity. See, for example: Misumi, S.; Kaneda, T. In "The Chemistry of the Carbon-Carbon Triple Bond"; Patai, S., Ed.; Wiley: New York, 1978; Chapter 16. Also: Muller, E.; Luppold, E.; Winter, W. *Synthesis* **1975**, 265 and references therein.

Interaction of Fischer Carbene Complexes of the Type W(CO)$_5$[C(OMe)R] (R = CH$_3$, C$_2$H$_5$) with Acetylenes

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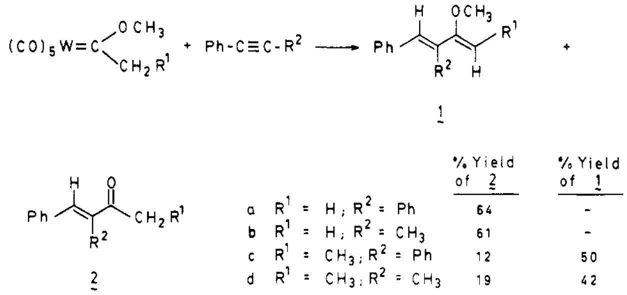
Summary: $W(CO)_5[C(OMe)CH_2R^1]$ (R^1 = H, CH_3) reacts with PhC_2R^2 (R^2 = Ph, CH_3) in toluene at 100 °C to give vinyl ethers and enones. The formation of these products can be explained by an exocyclic β-hydride elimination reaction of a metallacyclobutene intermediate.

Scheme I



		% Yield of 2	% Yield of 1
a	R^1 = H; R^2 = Ph	64	-
b	R^1 = H; R^2 = CH_3	61	-
c	R^1 = CH_3; R^2 = Ph	12	50
d	R^1 = CH_3; R^2 = CH_3	19	42

The interaction of Fischer-type chromium carbene complexes and acetylenes has received considerable attention from several research groups.[1-3] These investigations include mechanistic as well as synthetic studies, indicating that chromium carbene complexes have synthetic utility in the preparation of many useful organic molecules, including vitamins K and E,[4] nanomycin A and deoxyfrenolicin,[2] and precursors to anthracyclinones.[3] Surprisingly, little work has appeared concerning the interaction of Fischer-type tungsten carbene complexes with acetylenes.[5,6] The most recent report by Geoffroy and co-workers focused on the photochemistry of $W(CO)_5[C(OMe)Ph]$ with several acetylenes, including PhC_2Ph, PhC_2Me, MeC_2Me, PhC_2H, and *n*-$C_4H_9C_2H$.[5] The isolation of the first alkyne–carbene complex at −30 °C was also described by a photolysis of $W(CO)_5[C(OMe)Ph]$ and PhC_2Ph in hexane solvent.[5] We wish to report here our findings on the interaction of $W(CO)_5[C(OMe)CH_2R^1]$ (R^1 = H, CH_3) with acetylenes.

The carbene complexes $W(CO)_5[C(OMe)CH_2R^1]$ (R^1 = H,[7] CH_3[8]) were reacted with PhC_2R^2 (R^2 = Ph, CH_3) in toluene at 100 °C to produce **1c**, **1d**, and **2a–d** (Scheme I).[9,10] Compounds **1c**, **1d**, and **2a–d** were isolated by

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(1) For a comprehensive review see: Dötz, K. H. *Pure Appl. Chem.* **1983**, *55*, 1689.

(2) Semmelhack, M. F.; Bozell, J. J. *Tetrahedron Lett.* **1982**, *23*, 2931. Semmelhack, M. F.; Bozell, J. J.; Sato, T.; Wulff, W.; Spiess, E.; Zask, A. *J. Am. Chem. Soc.* **1982**, *104*, 5850.

(3) Wulff, W.; Peng-Cho, T.; McCallum, J. S. *J. Am. Chem. Soc.* **1981**, *103*, 7677. Wulff, W.; Peng-Cho, T. *Ibid.* **1984**, *106*, 434. Peng-Cho, T.; Wulff, W. *Ibid.* **1984**, *106*, 1132.

(4) Dötz, K. H. *J. Organomet. Chem.* **1977**, *140*, 177. Dötz, K. H.; Pruskil, I.; Mühlemeier, J. *Chem. Ber.* **1982**, *115*, 1278.

(5) Foley, H. C.; Strubinger, L. M.; Targos, T. S.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1983**, *105*, 3064.

(6) Katz, T. J.; Lee, S. J. *J. Am. Chem. Soc.* **1980**, *102*, 422. Katz, T. J.; Lee, S. J.; Shippey, M. A. *Ibid.* **1980**, *102*, 7940. Katz, T. J.; Lee, S. J. Shippey, M. A. *J. Mol. Catal.* **1980**, *8*, 219.

(7) Fischer, E. O.; Maasböl, A. *Chem. Ber.* **1967**, *100*, 2445. Aumann, R.; Fischer, E. O. *Ibid.* **1968**, *101*, 954.

(8) $W(CO)_5[C(OMe)C_2H_5]$ was prepared in 56% yield from ethyllithium and $W(CO)_6$ by using the same methods described in ref 7. The carbene prepared in this manner gave NMR and IR spectra in agreement with literature values. Winter, S. R.; Cornett, G. W.; Thompson, E. A. *J. Organomet. Chem.* **1977**, *133*, 339.

(9) All isolated compounds were characterized by ^1H NMR (400 MHz), ^{13}C NMR (100.6 MHz), MS, IR, and physical properties (mp, bp, R_f), which agreed with reported literature values. **2a**: Fine, S. A.; Pulaski, P. D. *J. Org. Chem.* **1973**, *38*, 1747. Zimmerman, H. E.; Singer, L.; Thyagarajan, B. S. *J. Am. Chem. Soc.* **1959**, *81*, 108. Veprek-Bilinski, V.; Narasimhand, K.; Dreiding, A. S. *Helv. Chim. Acta* **1978**, *61*, 3018. **2b** and **2d**: Roustan, J. L.; Guinot, A.; Cadiot, P. *J. Organomet. Chem.* **1980**, *194*, 367. **2c**: Unterhalt, B. *Arch. Pharm. Ber. Dtsch. Pharm.* **1967**, *300*, 748.

(10) Typically, 1.0 mmol of the tungsten carbene complex and 1.5–2.0 equiv of acetylene were used. The reactions were carried out in dry toluene under a nitrogen atmosphere. The reactions were terminated when the starting carbene complex had completely reacted as determined by TLC analysis.

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