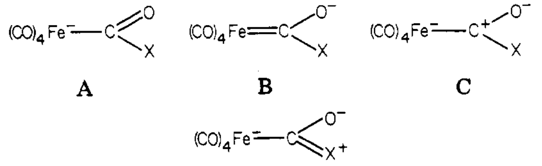
$(CO)_4Fe$ moiety bonded to a carbene ligand as expected for **6**.[12] A broad, medium intensity band at 1640 cm^{-1} can be assigned to the "ester" carbonyl group of **7**; a similar band appears in $CpFe(CO)_2COOMe$ at 1665 cm^{-1}.[11] The absorption bands of methyl acetate (ν(CO) = 1745 cm^{-1}) along with a band at 1815 cm^{-1} are already present as weak bands but grow to intense bands on a second run of the same sample, thus indicating ongoing decomposition of the initial complex. In the ν(CO) region the migration of the methyl group initiates a broad band centered at 2000 cm^{-1} along with an intense band at 1815 cm^{-1} due to bridging CO groups. $Fe_3(CO)_{12}$ was identified as a decomposition product of **7**, but the residue has not been studied further.

Anions of type **4** are basic and have two possible coordination sites for Lewis acids, one at the metal and the other at the alkoxycarbonyl or the carbamoyl oxygen atom. In contrast, the corresponding group 6B anions $M(CO)_5COOR^-$ (M = Cr, Mo, W) have only one site because two electrons at the metal are replaced by a CO group to achieve the rare-gas configuration. An attack of the electrophile at the metal is therefore not expected. The anion of **4b** may be compared with $S{=}C(O)OR^-$, in which S or O can be alkylated; similarities in chemical behavior of S and the $Fe(CO)_4$ group have been pointed out in a review.[13]

In spite of the two possible basic centers in **4**, the different behavior of **4a** and **4b** toward Me$^+$ is not fully understood. One explanation is that the replacement of the NR_2 group by OR causes a change in the basicity of the two sites. Considering the resonance structures A–D of the anion, it becomes apparent that a decreasing ability of X to back donation (going from X = NR_2 to X = OR) enhances the chance for an electrophile to react with the metal atom according to the minor contribution of form D.

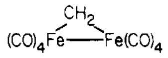


A B C

D

In contrast to this, a variety of salts of the type $[(CO)_4FeCOR]$ Li, mostly not isolated and used in situ, can be alkylated by $(Et_3O)BF_4$ to give the expected carbene complexes.[14] This communication reports the first example of the consecutive addition of a Lewis base and a Lewis acid to a binary transition-metal carbonyl that has not resulted in the formation of a Fischer-type carbene ligand.

The thermal decomposition of **7** via methyl group migration to the alkoxycarbonyl carbon atom to produce methyl acetate and iron carbonyl species can be regarded as a model reaction with respect to the chain growth sequence of the Fischer–Tropsch process.[15] A comparable methyl acetate formation has been observed by the reaction of the dinuclear complex **8** with MeOH at elevated temperatures; a μ-ketenyl complex was postulated as the reactive intermediate, generated by incorporation of a terminal CO group into the bridge.[16]



8

Homologation of a C_1 unit via rearrangement of a coordinated dimethoxycarbene ligand has not been reported. The free ligand, if generated from an organic source, dimerizes, and rearrangement to methyl acetate is only connected with special reaction conditions.[17] This feature and the spectroscopic data clearly indicate that the yellow alkylation product of **4b** has a structure as suggested for **7**. Further investigations concerning these systems are currently in progress.

Acknowledgment. This work was supported by the Fonds der Chemischen Industrie and by the DFG (Deutsche Forschungsgemeinschaft) with a grant to W.P.

Registry No. 4b, 58411-26-0; 7, 85883-27-8.

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$W(\eta^5\text{-}C_5H_5)[C(Ph)C(CMe_3)C(Ph)]Cl_2$: A Molecule Having a Localized, Nonplanar, Fluxional Metallacyclobutadiene Ring

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Summary: The reaction between $W(\eta^5\text{-}C_5H_5)(CCMe_3)Cl_2$ and disubstituted acetylenes yields tungstenacyclobutadiene complexes that in some cases exhibit a signal for essentially only one type of ring carbon atom on the NMR time scale at room temperature. One of these is the product with the composition $W(\eta^5\text{-}C_5H_5)(CCMe_3)(PhC{\equiv}CPh)Cl_2$. It crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ [C^5_{2h}; No. 14] with a = 9.859 (4) Å, b = 10.821 (2) Å, c = 20.580 (11) Å, β = 92.88 (4)°, V = 2193 Å^3, and ρ(calcd) = 1.72 g cm^{-3} for Z = 4 and M_r = 567.2. Convergence was achieved with R_F = 3.1% and R_{wF} = 2.6% for all 2599 data with 2θ(Mo Kα) = 4.5–45.0°. The WC_3 ring conformation is approximately halfway between a planar and tungstenatetrahedrane form with localized, alternating double and single bonds ($W{=}C_\alpha$ = 1.943 (5) Å, $C_\alpha{-}C_\beta$ = 1.485 (7) Å, $C_\beta{=}C_\alpha'$ = 1.372 (8) Å, $C_\alpha'{-}W$ = 2.132 (5) Å); the two phenyl rings are found on the α-carbon atoms. It is proposed that the alkylidyne fragments are scrambled on the metal via a fluxional process involving formation of a tungsten(VI) metallatetrahedrane or, alternatively, a tungsten(IV) cyclopropenyl intermediate.

Recently we showed[2] that the reaction between $W(CCMe_3)Cl_3$(1,2-dimethoxyethane) and 1 equiv of di-

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[1] (a) State University of New York at Buffalo. (b) Massachusetts Institute of Technology.
[2] Pedersen, S. F.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1982**, *104*, 6808.

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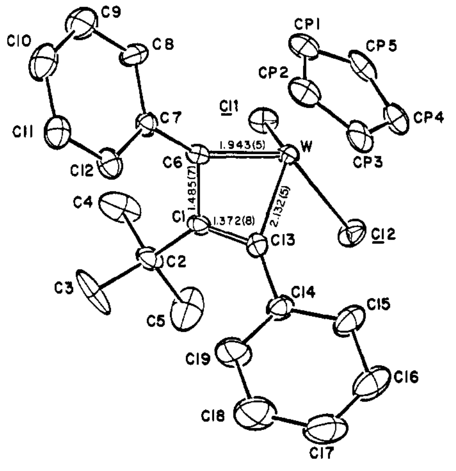


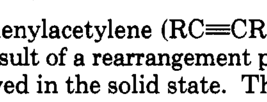
Figure 1. ORTEP-II drawing of $W(\eta^5\text{-}C_5H_5)[C(Ph)C(CMe_3)C(Ph)]Cl_2$ with hydrogen atoms omitted.

methylacetylene yields a tungstenacyclobutadiene complex, $W[C(CMe_3)C(Me)C(Me)]Cl_3$, an example of the suspected type of intermediate in the acetylene metathesis reaction catalyzed by complexes of the type $W(CR)(OCMe_3)_3$.[3] Until now we have assumed that the acetylene metathesis reaction consists of twice forming and cleaving a planar, configurationally stable tungstenacyclobutadiene ring. We show here that a tungstenacyclobutadiene ring need not be a planar, delocalized structure and that it may rearrange rapidly without losing acetylene.

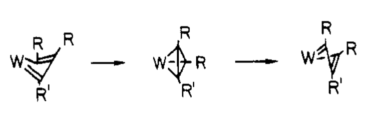
$W(\eta^5\text{-}C_5H_5)(CCMe_3)Cl_2$[4] can be made in high yield in three steps from $[Et_4N][W(CCMe_3)Cl_4]$.[5] It reacts with disubstituted acetylenes to give sparingly soluble compounds with the empirical formula $W(\eta^5\text{-}C_5H_5)(CCMe_3)(RC{\equiv}CR)Cl_2$ (R = Me, Et, *i*-Pr, Ph).[7] These products form quantitatively in the presence of 1 equiv or excess acetylene; only a trace of the metathesis product $Me_3CC{\equiv}CR$ is observed in the presence of excess acetylene. When R = Me or Et, the ^{13}C NMR spectra of the red products show *broad* signals for essentially two types of WC_3 ring carbon atoms[7] (cf. the ^{13}C NMR spectrum of unsymmetrical $W[C(CMe_3)C(R)C(R)]Cl_3$[2] where two signals are observed for the $C_\alpha R$ and $C_\alpha CMe_3$ carbon atoms at 267.5 and 263.4 ppm (or vv) and a signal is observed for the $C_\beta R$ carbon atom at 150.7[2]). However, when R = *i*-Pr or Ph only a single, broad, unsymmetrical ^{13}C NMR signal is observed for the WC_3 ring carbon atoms at ~175 and ~200 ppm, respectively, at 25 °C. The *i*-Pr and Ph complexes are green. On the basis of this ^{13}C NMR evidence alone one might conclude that the WC_3 rings are rapidly rearranging when R = *i*-Pr or Ph. The product of the reaction between $W(\eta^5\text{-}C_5H_5)(CCMe_3)Cl_2$ and $PhC{\equiv}CPh$ was chosen for an X-ray study since it crystallized well directly from the reaction mixture (in ether).[8]

The molecule illustrated in Figure 1 has a fairly normal "four-legged piano stool" coordination geometry about tungsten. Angles from "Cp" (the *centroid* of the $\eta^5\text{-}C_5H_5$ ligand) are Cp–W–Cl(1) = 113.68°, Cp–W–Cl(2) = 111.95°, Cp–W–C(6) = 111.23°, and Cp–W–C(13) = 120.66°. The W⋯Cp distance is 1.993 Å, and the tungsten–chloride bond lengths are 2.426 (2) and 2.442 (2) Å. The most unusual feature of the molecule is the nonplanar, localized form of the tungstenacyclobutadiene ring, in sharp contrast to the planar, delocalized geometry for the WC_3 ring in $W[C(CMe_3)C(Me)(C(Me)]Cl_3$.[2] The W–C(6) distance of 1.943 (5) Å is 0.189 (7) Å shorter than the W–C(13) bond length of 2.132 (5) Å. (For comparison, the W=C and W—C distances in $W(CCMe_3)(CHCMe_3)(CH_2CMe_3)(dmpe)$ are 1.942 (9) and 2.258 (9), respectively.[12]) The bond lengths C(1)–C(13) = 1.372 (8) Å and C(1)–C(6) = 1.485 (7) Å differ by 0.113 (11) Å and may be compared to the accepted values of C=C ≈ 1.34 Å and $C(sp^3)\text{-}C(sp^2) \approx 1.51$ Å. The WC_3 system is approximately halfway between a planar and metallatetrahedrane form as evidenced by the dihedral angles [W–C(6)–C(1)]/[W–C(13)–C(1)] = 54.59° and [C(6)–W–C(13)]/[C(6)–C(1)–C(13)] = 57.66°. The W–C(1) distance (2.339 (5) Å) is formally nonbonding. Angles within the WC_3 system are C(6)–W–C(13) = 65.18 (20)°, W–C(13)–C(1) = 80.58 (33)°, W–C(6)–C(1) = 84.93 (31)°, and C(6)–C(1)–C(13) = 100.70 (44)°, while the peripheral angles W–C(13)—C(14) = 143.74 (40)° and W=C(6)—C(7) = 148.48(39)° are unusually large, as was found also in the *planar* tungstenacyclobutadiene system.[2]

The basic structure of the ring in $W(\eta^5\text{-}C_5H_5)[C(Ph)C(CMe_3)C(Ph)]Cl_2$ is essentially that obtained by adding an acetylene to the midpoint of the tungsten–carbon triple bond, viz.



The added diphenylacetylene (RC≡CR) is subsequently "cleaved" as a result of a rearrangement process to give the structure observed in the solid state. The rearrangement process could consist of either "rotation" of an acetylene, e.g., exchange of C(1) and C(13) (Figure 1), or a phenomenologically closely related process involving formation of a tungsten(VI) metallatetrahedrane[3a,13] intermediate, viz.



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[4] Anal. Calcd for $WC_{10}H_{14}Cl_2$: C, 30.88; H, 3.63. Found: C, 31.03; H, 3.71. ^1H NMR (C_6D_6): δ 5.63 (s, 5, C_5H_5), 1.07 (s, 9, $CCMe_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 328.3 ($CCMe_3$), 106.3 (C_5H_5), 48.9 ($CCMe_3$), 32.4 ($CCMe_3$).

[5] $[NEt_4][W(CCMe_3)Cl_4]$[6] reacts with Me_3SiNEt_2 in dichloromethane to form $[NEt_4][W(CCMe_3)Cl_3(NEt_2)]$. $[NEt_4][W(CCMe_3)Cl_3(NEt_2)]$ reacts with TlCp in dichloromethane to yield $W(\eta^5\text{-}C_5H_5)(CCMe_3)Cl(NEt_2)$. $W(\eta^5\text{-}C_5H_5)(CCMe_3)Cl_2$ is then prepared by treating $W(\eta^5\text{-}C_5H_5)(CCMe_3)Cl(NEt_2)$ in pentane with 2 equiv of HCl. Reactions between $[W(CCMe_3)Cl_4]^-$ or $W(CCMe_3)Cl_2(dme)$ and TlC_5H_5 or NaC_5H_5 do not yield $W(\eta^5\text{-}C_5Me_5)(CCMe_3)Cl_2$.

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[7] For example, $W(\eta^5\text{-}C_5H_5)[C(Me)C(CMe_3)C(Me)]Cl_2$: ^1H NMR (C_6D_6) δ 4.98 (s, 5, C_5H_5), 3.41 (s, 6, Me), 1.19 (s, 9, CMe_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 244.3 (ring C_α), 120.4 (ring C_β), 99.1 (C_5H_5), 36.9 (CMe_3), 28.7 (CMe_3), 27.0 (Me). Anal. Calcd for $WC_{14}H_{20}Cl_2$: C, 37.95; H, 4.55. Found: C, 37.98; H, 4.66.

[8] The complex crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ [C_{2h}^5; No. 14] with a = 9.859 (4) Å, b = 10.821 (2) Å, c = 20.580 (11) Å, β = 92.88 (4)°, V = 2193 (2) Å^3, and ρ(calcd) = 1.72 g cm^{-3} for Z = 4 and M_r = 567.2. There is no crystallographic symmetry imposed upon the molecule. Diffraction data were collected on a Syntex $P2_1$ automated four-circle diffractometer via a coupled θ(crystal)–2θ(counter) scan technique[9] and were corrected for absorption (μ = 58.2 cm^{-1}). The structure was solved via a combination of direct methods (MULTAN[10]), difference Fourier, and full-matrix least squares refinement techniques. All non-hydrogen atoms were located and refined anisotropically, while hydrogen atoms were included in calculated positions (d(C–H) = 0.95 Å,[11] either in planar (sp^2) or staggered tetrahedral (sp^3) positions). Convergence was reached with R_F = 3.1% and R_{wF} = 2.6% for all 2599 data with 2θ(Mo Kα) = 4.5–45.0° (R_F = 2.4% and R_{wF} = 2.5% for those 2319 data with $|F_o| > 3\sigma(|F_o|)$).

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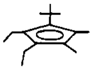
An alternative to a W(VI) metallatetrahedrane is a tungsten(IV) cyclopropenyl intermediate. We propose that this rearrangement process is rapid enough in W(η^5-C_5H_5)[C(R)C(CMe$_3$)C(R)]Cl$_2$ to average the ring carbon signals in the ^{13}C spectrum when R = *i*-Pr or Ph. When R = Me or Et, the rearrangement process, if it is occurring at all, is slower on the NMR time scale, perhaps as a result of differences in steric effects of the R groups.

It is likely that tungstenacyclobutadiene rings are fluxional in other systems. For example, we have found that 3-hexyne reacts with W[C(CMe$_3$)C(Me)C(Me)](OCMe$_2$CMe$_2$O)(OCMe$_3$) to give not only products containing the type of cyclopentadienyl ring (A) we would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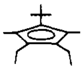
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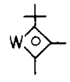
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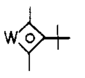

D

expect if 3-hexyne had inserted into the W–C$_\alpha$ or W–C$_\alpha$′ bond, but also a second, more symmetrically substituted ring (B). Only these two rings are formed in a ratio of 6:4 (A:B) in W[η^5-C_5(CMe$_3$)Me$_2$Et$_2$]Cl$_4$[2,14] and 4:6 in W[η^5-C_5(CMe$_3$)Me$_2$Et$_2$]O$_2$(OCMe$_3$).[2] Although there are other possibilities, the explanation we prefer is that the C metallacycle can rearrange rapidly to the D metallacycle in the hypothetical acetylene adduct, e.g., W[C(CMe$_3$)C(R)C(R)]Cl$_3$(R′C≡CR′) → W[C(R)C(CMe$_3$)C(R)]Cl$_3$(R′C≡CR′). We are exploring the possibility that rearrangement of tungstenacyclobutadiene rings is an integral feature of the acetylene metathesis reaction.[3]

Acknowledgment. We thank the National Science Foundation for supporting this research (Grants CHE 81-21282 to R.R.S. and CHE 80-23448 to M.R.C.). L.M. thanks the Halcon Corp. for fellowship support for the period 1982–1983.

Registry No. W(η^5-C_5H_5)(CCMe$_3$)(MeC≡CMe)Cl$_2$, 85957-17-1; W(η^5-C_5H_5)(CCMe$_3$)(EtC≡CEt)Cl$_2$, 85957-18-2; W(η^5-C_5H_5)(CCMe$_3$)(*i*-PrC≡CPr-*i*)Cl$_2$, 85957-19-3; W(η^5-C_5H_5)(CCMe$_3$)(PhC≡CPh)Cl$_2$, 85957-20-6; W(η^5-C_5H_5)(CCMe$_3$)Cl$_2$, 85957-21-7; [NEt$_4$][W(CCMe$_3$)Cl$_4$], 78251-20-4; [NEt$_4$][W(CCMe$_3$)Cl$_3$(NEt$_2$)], 85957-23-9; W(η^5-C_5H_5)(CCMe$_3$)Cl(NEt$_2$), 85957-24-0; TlCp, 34822-90-7; MeC≡CMe, 503-17-3; EtC≡CEt, 928-49-4; *i*-PrC≡CPr-*i*, 927-99-1; PhC≡CPh, 501-65-5; Me$_3$SiNEt$_2$, 996-50-9.

Supplementary Material Available: Listings of positional parameters and observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.

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(14) Paramagnetic W[η^5-C_5(CMe$_3$)Me$_2$Et$_2$]Cl$_4$ reacts with Zn(CH$_2$CMe$_3$)$_2$ to give diamagnetic W[η^5-C_5(CMe$_3$)Me$_2$Et$_2$](CCMe$_3$)Cl$_2$.[15] Ring structures A and B were assigned on the basis of ^{1}H and ^{13}C NMR spectra and the assumption that the ethyl groups are adjacent to one another.

(15) Holmes, S. J.; unpublished results.

Basic Cluster Reactions. 5.[1] Capping Reactions of RuCo$_2$(CO)$_{11}$

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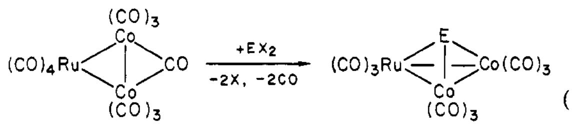
Received April 20, 1983

Summary: The cluster RuCo$_2$(CO)$_{11}$ reacts under mild conditions with a wide variety of reagents that can act as precursors of four-electron fragments, leading to capping of the RuCo$_2$ triangle with formation of the μ_3-bridged compounds RuCo$_2$(CO)$_9$E (E = PR, AsR, S, Se, R$_2$C$_2$, Cp(CO)FeC$_2$R, Cp(CO)W≡CR, Ru(CO)$_4$, Co(CO)$_3^-$).

The extension of metal complex chemistry brought about by transition-metal clusters rests on two basic cluster properties: the availability of the metal–metal bonds as reactive sites[2] and the possibility of substrate binding to more than one metal atom.[3] The latter situation is quite common for μ_3 substrate binding, i.e., capping of metal atom triangles.[4] However capping *reactions*, i.e., designed attachments of μ_3 ligands to metal triangles, are not common since they normally require the removal of more than one terminal ligand. And only for the unsaturated cluster H$_2$Os$_3$(CO)$_{10}$ have several different types of capping reactions been found.[3,4] We have now observed that the saturated cluster RuCo$_2$(CO)$_{11}$,[5] due to the combined lability of its Co– and Ru–CO ligands, is suitable for all kinds of capping.

Each of the reactions involves the attachment of a four-electron μ_3 ligand on top of the RuCo$_2$ triangle with elimination of two CO ligands. If the capping unit E has a main-group element as the μ_3 atom, the corresponding reagent has to be bifunctional and bear an unshared electron pair on E. The reactions are according to eq 1, as performed for PR, AsR, S, and Se capping.



(1)

1, E = PMe
2, E = AsMe
3, E = S
4, E = Se

In a typical experiment a solution of AsMeH$_2$ (35 mg, 0.38 mmol) in benzene (10 mL) was added dropwise within 20 min to RuCo$_2$(CO)$_{11}$ (200 mg, 0.38 mmol) in hexane (40 mL) at 0 °C. After filtration and chromatography of the reaction mixture on a silica gel column, RuCo$_2$(CO)$_9$AsMe (2, 80 mg, 38%) was obtained as dark brown crystals, mp >250 °C dec; δ(^{1}H, benzene) 2.03; ν(CO, cyclohexane) 2091 (w), 2069 (vw), 2051 (vs), 2042 (vs), 2027 (s), 2012 (w), 1982 (w) cm^{-1}. The clusters 1, 3, and 4 (cf. Table I) whose IR spectra are very similar were obtained accordingly.

Acetylenes are four-electron ligands in themselves. It was not surprising, therefore, that Ph$_2$C$_2$ reacted at room temperature with RuCo$_2$(CO)$_{11}$ to form RuCo$_2$(CO)$_9$(Ph$_2$C$_2$) (5). However the metal acetylide Cp(CO)$_2$FeC$_2$Ph[6] and the metal carbyne Cp(CO)$_2$W≡C(tol)[7] were incorporated at room temperature as well with formation of 6 and 7. In a characteristic reaction Cp(CO)$_2$W≡C(tol) (200 mg, 0.49 mmol) and RuCo$_2$(CO)$_{11}$ (200 mg, 0.38 mmol) in hexane (50 mL) were stirred for 1 h, raising the temper-

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(1) Part 4: Roland, E.; Fischer, K.; Vahrenkamp, H. *Angew. Chem.* **1983**, *95*, 324; *Angew. Chem.; Int. Ed. Engl.* **1983**, *22*, 326.

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