An alternative to a W(VI) metallatetrahedrane is a tungsten(IV) cyclopropenyl intermediate. We propose that this rearrangement process is rapid enough in $W(\eta^5-C_5H_5)$ [C- $(R)C(CMe_3)C(R)]Cl_2$ to average the ring carbon signals in the ¹³C 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 $W[C(CMe_3)C(Me)C(Me)]$ -(OCMe₂CMe₂O)(OCMe₃) to give not only products containing the type of cyclopentadienyl ring (A) we would



expect if 3-hexyne had inserted into the W-C_a or W-C_a' 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 $W[\eta^5-C_5(CMe_3)Me_2Et_2]Cl_4^{2,14}$ and 4:6 in $W[\eta^5-C_5(CMe_3)Me_2Et_2]Cl_4^{2,14}$ $C_5(CMe_3)Me_2Et_2]O_2(OCMe_3)$.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., $W[C(CMe_3)C (R)C(R)]Cl_3(R'C \equiv CR') \rightarrow W[C(R)C(CMe_3)C(R)]Cl_3$ $(R'C \equiv CR')$. We are exploring the possibility that rearrangement of tungstenacyclobutadiene rings is an integral feature of the acetylene metathesis reaction.³

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Registry No. $W(\eta^5-C_5H_5)(CCMe_3)(MeC \equiv CMe)Cl_2, 85957 C_5H_5$)(CCMe₃)(*i*-PrC=CPr-*i*)Cl₂, 85957-19-3; W(η^5 -C₅H₅)- $\begin{array}{l} (CCMe_3)(PhC = CPh)Cl_2, \ 85957-20-6; \ W(\eta^5-C_5H_5)(CCMe_3)Cl_2, \\ 85957-21-7; \ [NEt_4][W(CCMe_3)Cl_4], \ 78251-20-4; \ [NEt_4][W-(CCMe_3)Cl_3(NEt_2)], \\ 85957-23-9; \ W(\eta^5-C_5H_5)(CCMe_3)Cl(NEt_2), \\ \end{array}$ 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; Me₃SiNEt₂, 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.

(14) Paramagnetic $W[\eta^5-C_5(CMe_3)Me_2Et_2]Cl_4$ reacts with Zn-(CH₂CMe₃)₂ to give diamagnetic $W[\eta^5-C_5(CMe_3)Me_2Et_2](CCMe_3)Cl_2$.¹⁵ Ring structures A and B were assigned on the basis of ¹H and ¹³C NMR spectra and the assumption that the ethyl groups are adjacent to one another

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Basic Cluster Reactions. 5.1 Capping Reactions of RuCo₂(CO)₁₁

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Summary: The cluster RuCo₂(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 RuCo₂ triangle with formation of the μ_3 -bridged compounds $RuCo_2(CO)_9E$ (E = PR, AsR, S, Se, R_2C_2 , $Cp(CO)FeC_2R$, $Cp(CO)W \equiv CR$, $Ru(CO)_4$, $Co(CO)_3^-$).

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 sites² 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 $H_2Os_3(CO)_{10}$ have several different types of capping reactions been found.^{3,4} We have now observed that the saturated cluster $\operatorname{RuCo}_2(\operatorname{CO})_{11}$,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 RuCo₂ 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.



In a typical experiment a solution of AsMeH₂ (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, $RuCo_2(CO)_9AsMe$ (2, 80 mg, 38%) was obtained as dark brown crystals, mp >250 °C dec; δ (¹H, 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_2C_2 reacted at room temperature with $RuCo_2(CO)_{11}$ to form $RuCo_2(CO)_{9}$ - (Ph_2C_2) (5). However the metal acetylide $Cp(CO)_2FeC_2Ph^6$ and the metal carbyne $Cp(CO)_2W \equiv C(tol)^7$ were incorporated at room temperature as well with formation of 6 and 7. In a characteristic reaction Cp(CO)₂W=C(tol) (200 mg, 0.49 mmol) and RuCo₂(CO)₁₁ (200 mg, 0.38 mmol) in hexane (50 mL) were stirred for 1 h, raising the temper-

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Table I. Capping Reagents and Products¹⁰

reagent	temp, °C	pro- duct	yield, %
MePH,	-20 to + 20	1	37
MeAsĤ,	0	2	38
EtSH	20	3	31
Ph,Se,	20	4	22
Ph ₂ C ₂	20	5	73
Cp(CO), FeC, Ph	20	6	69
Cp(CO), WC(tol)	-20 to $+20$	7	12
RuCo ₂ (CO) ₁₁ (decomp) ⁵	35	8	46
KCo(CO) ₄ /H ₃ PO ₄	0 to + 20	9	56

ature from -15 to +20 °C. Chromatography on a silica gel column afforded first $Co_2WCp(CO)_8C(tol)^8$ and then 7 (40 mg, 12%) as black crystals: mp 196 °C, δ (¹H, CDCl₃): Me 2.34, Cp 5.39, C₆H₄ 7.31 (m); v(CO, CHCl₃) 2076 (s), 2032 (vs), 2008 (m) 1992 (m), 1860 (w, br), 1795 (w, br) cm⁻¹. Metal carbonyl fragments are equally well suited for the



capping reaction. This had been observed in the thermal decomposition reaction of $RuCo_2(CO)_{11}^5$ where it is likely that $Ru(CO)_n$ fragments are liberated and then added with formation of $Ru_2Co_2(CO)_{13}$ (8). It was now used for the preparation of $\operatorname{RuCo}_3(\operatorname{CO})_{12}^-$ by addition of $\operatorname{KCo}(\operatorname{CO})_4$ in THF and subsequent acidification to give a 56% yield of HRuCo₃(CO)₁₂ (9).⁹ All capping reactions are summarized in Table I.¹⁰

Although $RuCo_2(CO)_{11}$ is saturated according to the 18-electron rule, it reacts like an unsaturated compound. This is an illustration of the driving force inherent in the capping reaction which in this specific case is made easy by the CO lability on cobalt as well as on ruthenium. It makes possible the elimination of organic substitutents from sulfur and selenium, i.e., the formation of 3 and 4, which normally requires forcing conditions. And it allows the uncomplicated low-temperature incorporation of reactive units like acetylenes or metal carbonyl reagents to form new clusters whose thermal stability is limited. It is likely that all these capping reactions start with CO substitution. The tendency for capping rather than fragmentation or μ bridging of the cluster must have to do with the fact that the resulting compounds all have a $M_3(CO)_9X$ composition which seems to be especially preferred in metal carbonyl chemistry due to its ideal stereochemical and possibly electronic situation.

The use of the starting cluster $RuCo_2(CO)_{11}$ is favorable in this context since many capping units are four-electron ligands which just means that a $RuCo_2(CO)_9X$ composition will result in the form of the stable compounds 1-9. By contrast, the tendency for capping may be an important aspect in the field of substrate activation by clusters where it is essential to fix but not passivate reaction intermediates in a stereochemically and electronically suitable environment. The interconversions of C-N compounds capping

a Fe₃(CO)₉ unit¹¹ and the first $M_3(CO)_9(HCCR) \rightarrow M_3$ - $(CO)_9(CCHR)$ isomerizations¹² may serve as examples.

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Registry No. 1, 86272-85-7; 2, 86272-86-8; 3, 86272-87-9; 4, 86272-88-0; 5, 86288-23-5; 6, 86272-89-1; 7, 86272-90-4; 9, 24013-40-9; RuCo₂(CO)₁₁, 78456-89-0; MePH₂, 593-54-4; MeAsH₂, 593-52-2; Ph₂Se₂, 1666-13-3; EtSH, 75-08-1; Co, 7440-48-4; Ru, 7440-18-8; Fe, 7439-89-6; W, 7440-33-7.

Supplementary Material Available: Tables containing the IR and NMR data, the melting points, and the elemental analyses of the new compounds 1-7 and crystallographic details and figures of the molecular structures of 5-7 (6 pages). Ordering information is given on any current masthead page.

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Characterization and Interconversion of Metal-Phosphorus Single and Double Bonds: Bis(cyclopentadienyl)zirconium and -hafnium Bis(dlorganophosphide) Complexes[†]

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Summary: Two equivalents of LiPR₂ react with (η - $C_5H_5)_2MCI_2$, affording $(\eta-C_5H_5)_2M(PR_2)_2$ (M = Zr, Hf; R = ethyl, cyclohexyl (Cy), or phenyl). ³¹P NMR and X-ray structural results indicate that these complexes contain both single and double metal-phosphorus bonds which interconvert in solution. Sodium naphthalenide reduction of these complexes produces the corresponding Zr^{III} and Hf^{III} complexes $[(\eta - C_5H_5)_2M(PR_2)_2][Na(THF)_n]$; a bis(μ diorganophosphido) heterobimetallic structure is proposed.

Early transition-metal complexes containing terminal diorganoamide ligands have a well-developed preparative and derivative chemistry,^{1,2} but the phosphorus analogs do not.²⁻⁷ Both examples^{2,3} of structurally characterized

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[†]Contribution No. 3207.

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