Directed synthesis of dimetallacyclobutenes: reaction of M(CO)4(.eta.2-CF3C.tplbond.CCF3) (M = ruthenium, osmium) with other 18-electron species

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in the order of compounds Cp*WOMe₃, Cp*WO(O₂)Me, and Cp*WO₂Me thus follows increasing C sp³ and W 5d overlap.

In contrast to the reactivity of the (trimethylsilyl)methyl complexes,[5] heat or irradiation did not effect conversion of Cp*WOMe₃ to Cp*WO(=CH₂)CH₃. However, both **3** and **4** apparently act as O transfer agents. Transfer of O from the peroxy compounds to substrates, such as phosphines or olefins, might be anticipated by analogy with Mimoun's work with peroxo molybdenum complexes.[2] We are investigating these possibilities with **3**, **4**, and other analogous chiral peroxides. Although O transfers readily from **3** or **4** to triphenylphosphine at room temperature (<10 min) regenerating **2** or Cp*WO₂CH₂SiMe₃, respectively, we have not yet achieved olefin epoxidations with these tungsten complexes. The thermodynamic stability of both **2** and **3** and presumably their molybdenum analogues would suggest that a catalytic O-atom transfer system could be developed with these systems.

Supplementary Material Available: Tables of experimental procedure, atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and calculated hydrogen positions and a complete figure with labels (10 pages); a listing of observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

Directed Synthesis of Dimetallacyclobutenes: Reaction of M(CO)₄(η²-CF₃C≡CCF₃) (M = Ru, Os) with Other 18-Electron Species

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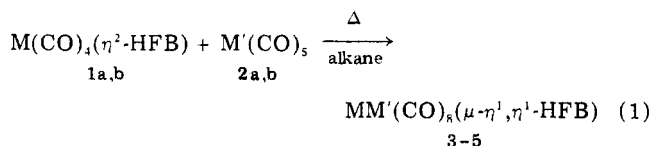*Edmonton, Alberta, Canada T6G 2G2*

Summary: Reflecting the strong π-acceptor nature of hexafluorobut-2-yne (CF₃C≡CCF₃, HFB), the compounds M(CO)₄(η²-HFB) (M = Ru, Os) readily react with other 18-electron species, such as M'(CO)₅ (M' = Ru, Os) and Cp*M''(CO)₂ (M'' = Co, Rh, Ir; Cp* = C₅Me₅), to give the corresponding dimetallacyclobutenes in good yields.

The chemistry of di- and polynuclear transition-metal alkyne complexes continues to attract a great deal of attention in view of the central role that these complexes occupy in mapping out intermediate steps in alkyne coupling reactions[1] and in providing realistic models for the adsorption and further transformation of surface-bound

alkynes.[2] The usual methodology for the synthesis of these species is the reaction of alkynes with preformed multicenter complexes.[3] Only recently has a report[4] appeared on the designed synthesis of bimetallic alkyne complexes from a mononuclear starting material. The products were interesting examples of heterodimetallate-trahedranes (i.e., dimetallic complexes containing a μ-η²,η² or perpendicular alkyne bridge[5]). Here we wish to report another example of such a directed synthesis, which however gives rise to dimetallacyclobutenes (i.e., molecules with a μ-η¹,η¹ or parallel alkyne bridge[5]).

In a continuation of our efforts to synthesize simple alkyne–tetracarbonyl derivatives of the iron triad transition metals,[6] the photoreaction of M(CO)₅ (M = Ru, Os) with hexafluorobut-2-yne (CF₃C≡CCF₃, HFB) was carried out. Careful control of the reaction conditions and isolation procedure, especially with ruthenium, gave the respective M(CO)₄(η²-HFB) (M = Ru, **1a**; M = Os, **1b**) compounds in good yields.[7] Both **1a** and **1b** are extremely volatile, white crystalline materials that can be handled at room temperature, in air for short periods of time. The stability increase of **1a** over its bis(trimethylsilyl)acetylene analogue[6] is noteworthy and reflects the strong π-acceptor nature of HFB. The latter feature is also responsible for the absence of axial–equatorial carbonyl exchange in both **1a** and **1b** at room temperature and above.

In a remarkable development we discovered that the 18-electron complexes M(CO)₄(η²-HFB) (**1a** and **1b**) react further with M'(CO)₅ (M' = Ru, Os) to give the corresponding dimetallacyclobutenes in good yields[8] (eq 1).

$$M(CO)_4(\eta^2\text{-HFB}) + M'(CO)_5 \xrightarrow[\text{alkane}]{\Delta}$$
$$\text{1a,b} \qquad\qquad \text{2a,b}$$

$$MM'(CO)_8(\mu\text{-}\eta^1,\eta^1\text{-HFB}) \quad (1)$$
$$\text{3-5}$$

			Δ	yield
1a, M = Ru	**2a**, M' = Ru	**3**, MM' = Ru₂	25 °C	73%
1b, M = Os	**2b**, M' = Os	**4**, MM' = Os₂	60 °C	66%
1a M = Ru	**2b**, M' = Os	**5**, MM' = RuOs	25 °C	77%

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(7) In a typical experiment 100–200 mg of M(CO)₅ and excess HFB dissolved in pentane is photolyzed with filtered radiation (λ ≥ 340 nm) in an immersion type apparatus at -20 °C. The progress of the reaction is followed by IR spectroscopy. At the end of the reaction, the solution is slowly concentrated at low temperature and the product is crystallized at -78 °C. A yield of over 80% can be obtained. Alternatively, after the solvent is removed completely, the products may be purified by room temperature bulb-to-bulb sublimation in a closed vacuum system, the receiving flask being kept at dry-ice temperature. The latter method may become necessary in the ruthenium reaction that is sometimes accompanied by the formation of byproducts, such as Ru(CO)₄(HFB)₂. Fuller details on the synthesis and properties, including X-ray structures, of M(CO)₄(η²-HFB) compounds will appear in a forthcoming publication. Spectral and analytical data on compounds **1a**, **1b**, **3**, **4**, **5**, **7**, **8**, and **9** are listed in the supplementary material.

(8) The OsOs compound **4**, obtained via thermal exchange reaction between Os₂(CO)₈[μ,η¹,η¹-CH₂CH(CO₂Me)] and CF₃C≡CCF₃, has been described before (Burke, M. R.; Takats, J. *J. Organomet. Chem.* **1986**, *302*, C25). However the yield of **4** was low and erratic.
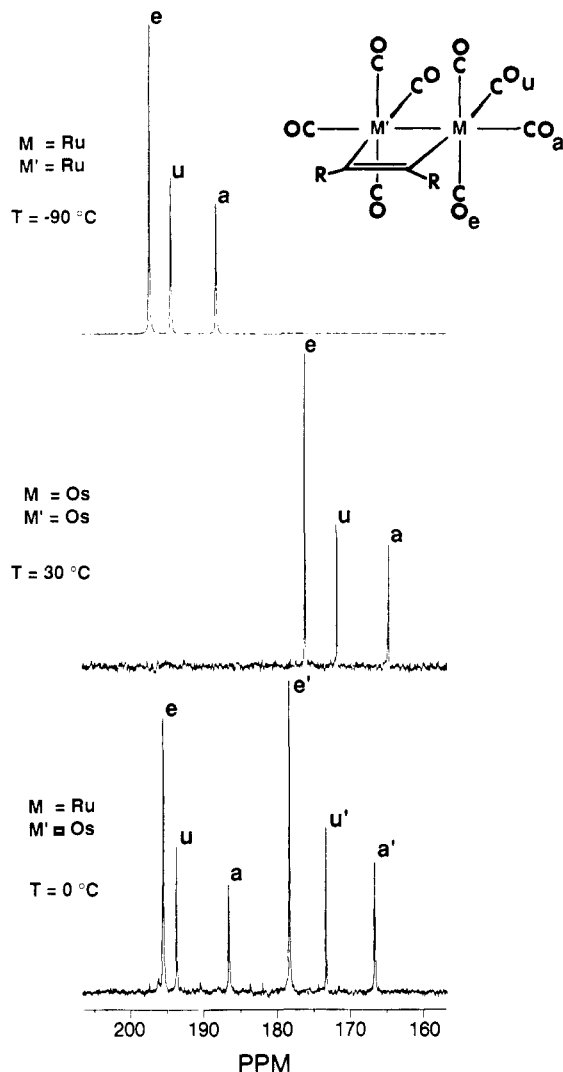
Figure 1. Low-temperature-limiting ^{13}C NMR spectra of $MM'(CO)_8(\mu-\eta^1,\eta^1\text{-HFB})$.

Especially spectacular was the reaction of $Ru(CO)_4(\eta^2\text{-HFB})$ with $Os(CO)_5$. When pentane solutions of **1a** and **2b** are mixed at room temperature, an almost immediate precipitation of **5** was observed. The formation of the other complexes was just as straightforward except requiring longer reaction times for **3** and higher temperatures for compound **4**.

The proper formulation of the complexes was ascertained by spectroscopic techniques, the ^{13}C NMR spectra being especially valuable. The limiting spectra are shown in Figure 1. The number and intensity distribution of the peaks are clearly consistent with the proposed structures. The spectra also provide a nice illustration of the predictable upfield shifts of the carbonyl signals as the metal triad is descended.[9] As anticipated from the different temperatures needed to observe the limiting spectra, the molecules are fluxional. Indeed the respective assignment of the axial (CO_a) and the unique (CO_u) carbonyl groups in the spectra was made on the basis of their temperature-dependent behavior. This is depicted for the RuOs compound in Figure 2. The most plausible mechanism for the intermetallic exchange of the carbonyl groups is the well-known "merry-go-round" process[10] which ex-
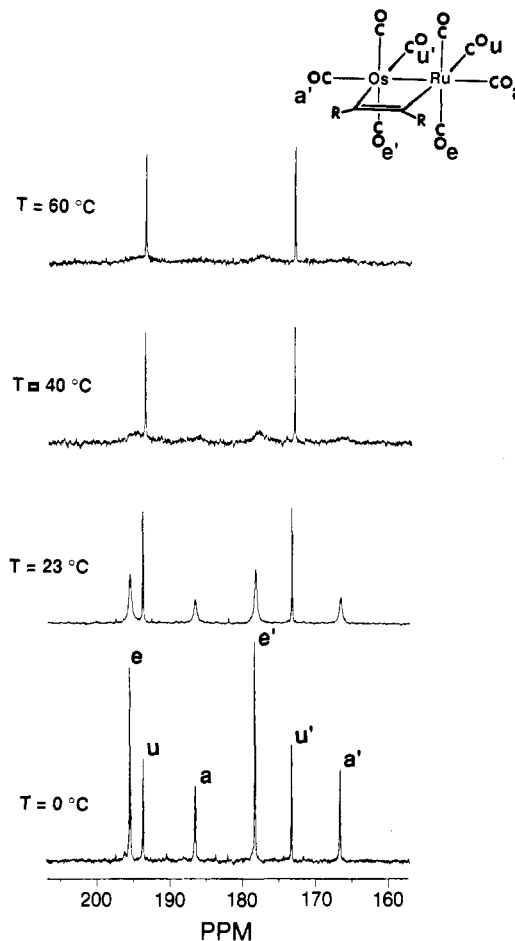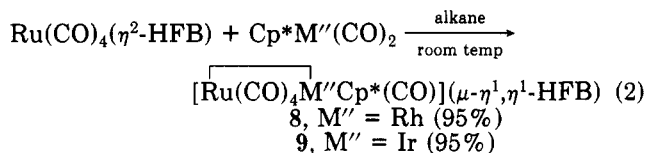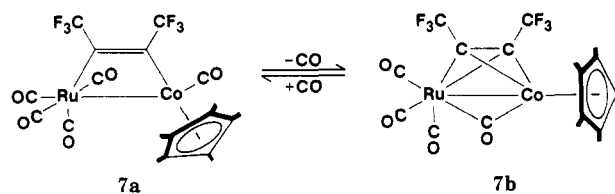
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Figure 2. Variable-temperature ^{13}C NMR spectra of $RuOs(CO)_8(\mu-\eta^1,\eta^1\text{-HFB})$.

changes environments of carbonyls lying in a plane, leaving one, the unique CO trans to the parallel alkyne bridge, invariant. The activation energy for the interchange follows RuRu (11.0 kcal/mol) < RuOs (14.4 kcal/mol) < OsOs (static at room temperature).

As a first step toward establishing the utility of these alkyne complexes as a means to forming other heterodimetallacyclobutenes, the reaction of **1a** with $Cp^*M''(CO)_2$ ($M'' = Co$, **6a**; $M'' = Rh$, **6b**; $M'' = Ir$, **6c**; $Cp^* = C_5Me_5$) was investigated. As shown in eq 2 the reaction with Rh

$$Ru(CO)_4(\eta^2\text{-HFB}) + Cp^*M''(CO)_2 \xrightarrow[\text{room temp}]{\text{alkane}}$$

$$[Ru(CO)_4M''Cp^*(CO)](\mu-\eta^1,\eta^1\text{-HFB}) \quad (2)$$
$$\textbf{8}, M'' = Rh \ (95\%)$$
$$\textbf{9}, M'' = Ir \ (95\%)$$

and Ir gives the desired complexes in excellent yields. Although the reaction with Co is more complicated, it also reveals another interesting potential of these compounds. Instead of pure heterodimetallacyclobutene, **7a**, the reaction between **1a** and **6a** gave a mixture of this and the related heterodimetallatetrahedrane **7b**. As shown in eq 3 the two compounds are easily interconverted. Indeed

7a   **7b**

(3)

if reaction 2 is carried out under nitrogen purge, pure **7b** is obtained directly and in yields exceeding 90%. Atmospheric carbonylation of **7b** readily gives **7a**, and this two-step sequence is the preferred route to this compound. Similar interconversion in a related dirhodium system has been well-documented by Dixon et al.,[11] who have also chronicled the rich derivatives chemistry of [(η-C$_5$H$_5$)$_2$Rh$_2$(CO)](μ-η^2,η^2-HFB).[12]

Clearly the M(CO)$_4$(η^2-HFB) complexes show great promise toward the synthesis of a variety of dimetallacyclobutenes. The scope of the reaction, the conversion of the compounds to the corresponding dimetallatetrahedranes and their further derivatization as well as the mechanism[13] of reactions 1 and 2 are being actively pursued in our laboratories.

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(12) Dickson, R. S.; Fallon, G. D.; Jenkins, S. M.; Nesbit, R. J. *Organometallics* **1987**, *6*, 1240 and references therein.

(13) Although reactions 1 and 2 are initiated by two 18-electron species, it is clear that the intimate mechanism of product formation proceeds via the intermediacy of a 16-electron intermediate. The strong π-acceptor nature of HFB favors reversible loss of CO from **1a** and **1b** as the first step of the reaction. This assumption is consistent with the rapid exchange of the carbonyl ligands of **1a** with ^{13}CO and is further strengthened by the preliminary observation that the reaction of Ru-(^{13}CO)$_4$(η^2-HFB) with Os(CO)$_5$ gives RuOs[(^{13}CO)$_3$(CO)$_5$](μ-η^1,η^1-HFB). The relative ease of reaction 1 is also supportive of this idea. The speed of the reaction is **1a** with **2b** > **1a** with **2a** > **1b** with **2b** and reflects the fact that the putative intermediate, M(CO)$_3$(HFB), is easier to achieve with Ru than Os. The observation that **1a** reacts more readily with **2b** than **2a** is in accord with the greater basicity of the former and its, now well-recognized, ability to partake in donor–acceptor metal–metal bond formation.[14] It is interesting to note that in addition to helping the dissociation of CO from **1a** and **1b**, the HFB ligand, by virtue of its ability to function as a 4-electron donor, also stabilizes the presumed M(CO)$_3$-(HFB) intermediate. Efforts are underway to isolate and characterize such species.

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Selective Formation of Titanium Enolates from Ketones and Bis(pentamethylcyclopentadienyl)dimethyltitanium-(IV)[1a]

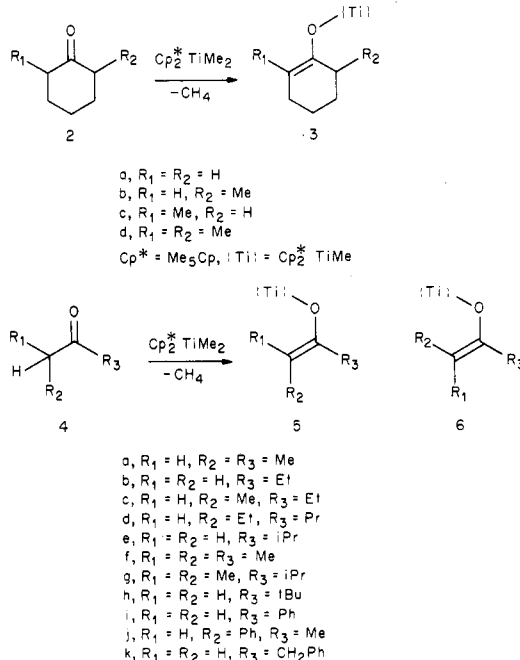**Steven H. Bertz,** **Gary Dabbagh, and Charles P. Gibson**[1b]

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Summary: A variety of ketones react with (η^5-C$_5$Me$_5$)$_2$Ti=CH$_2$, formed in situ by thermolysis of the title compound, to yield Ti enolates in a process that is highly regioselective and extraordinarily stereoselective.

Enolates are among the most important synthetic intermediates due to the variety of C–C bond-forming reactions and other functionalizations they mediate. Following the pioneering studies of Stork and Hudrlik[2] and House et al.,[3] Li enolates have been the most widely used; however, there has been growing interest in the use of other metals[4] in order to obtain improved selectivity. We wish to report the preparation of Ti enolates from ketones and bis(η^5-pentamethylcyclopentadienyl)dimethyltitanium(IV) (**1**)[5] with regioselectivity comparable to hindered amide bases and the best stereoselectivity yet observed.

As summarized in Table I, good to excellent yields of enolates result when the corresponding ketones are heated at 100 °C with a slight excess of **1** in toluene in a sealed tube (or under a static Ar atmosphere). For example 2-methylcyclohexanone (**2b**) yielded 87% of the less substituted enolate **3b** and <0.5% of the more substituted one **3c**. When **2b** was treated with lithium diisopropylamide (LDA) and trimethylsilyl chloride, a 99:1 ratio of less substituted to more substituted trimethylsilyl enol ethers was obtained.[3] With excess **2b**, the mixture of enolates **3b** + **3c** observed initially was converted completely to **3c** by continued heating (48 h at 100 °C). No enolate **3d** was detected when the substrate was 2,6-dimethylcyclohexanone (**2d**). In the acyclic series, methyl isopropyl ketone (**4e**) afforded an 86:3 ratio of yields of less substituted (**5e**) to more substituted (**5f**) enolates. The minor enolate (**5f**) is probably not formed directly from **4e**, as diisopropyl ketone (**4g**) yielded no detectable enolate **5g**.

2 → **3**

a, R$_1$ = R$_2$ = H
b, R$_1$ = H, R$_2$ = Me
c, R$_1$ = Me, R$_2$ = H
d, R$_1$ = R$_2$ = Me

Cp* = Me$_5$Cp, |Ti| = Cp$_2^*$TiMe

4 → **5**, **6**

a, R$_1$ = H, R$_2$ = R$_3$ = Me
b, R$_1$ = R$_2$ = H, R$_3$ = Et
c, R$_1$ = H, R$_2$ = Me, R$_3$ = Et
d, R$_1$ = H, R$_2$ = Et, R$_3$ = Pr
e, R$_1$ = R$_2$ = H, R$_3$ = iPr
f, R$_1$ = R$_2$ = R$_3$ = Me
g, R$_1$ = R$_2$ = Me, R$_3$ = iPr
h, R$_1$ = R$_2$ = H, R$_3$ = tBu
i, R$_1$ = R$_2$ = H, R$_3$ = Ph
j, R$_1$ = H, R$_2$ = Ph, R$_3$ = Me
k, R$_1$ = R$_2$ = H, R$_3$ = CH$_2$Ph

Although methyl ethyl ketone (**4a**) afforded a mixture of all three possible enolates (**5a**, **6a**, and **5b**), diethyl ketone (**4c**) and dipropyl ketone (**4d**) each yielded only a single enolate (**5c** and **5d**, respectively) within the limit of

(1) (a) New Titanium Chemistry. 1. For part 2 see: Gibson, C. P.; Dabbagh, G.; Bertz, S. H. *J. Chem. Soc., Chem. Commun.*, in press. (b) Current address: Department of Chemistry, West Virginia University, Morgantown, WV 26505.

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