Acknowledgment. We thank Arthur Smith for assistance in synthesizing I. This work was done while P.D. was a Visiting Scientist at Xerox. He thanks the members of Webster Research Center for their hospitality.

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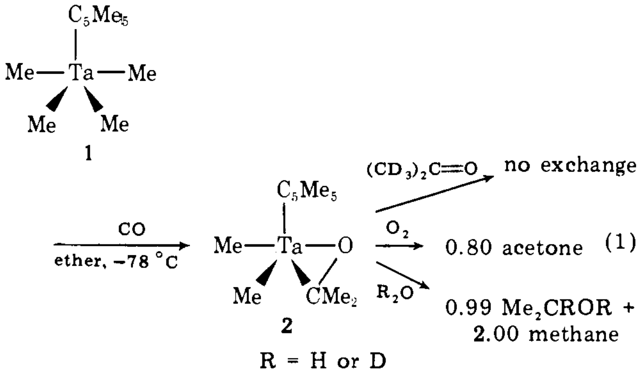
Reaction of CO with Ta(η^5-C_5Me_5)Me_4. Intramolecular Reductive Coupling of Carbon Monoxide via an "η^2-Acetone" Intermediate

Sir:

Since one of the most sought after catalytic reactions today is the selective reductive coupling of two molecules of CO with H_2,[1,2] it is important to know under what circumstances and how CO carbon atoms couple. One documented method consists of coupling oxycarbene-like Zr acyl ligands.[3,4] We report here another using Ta (η^5-C_5Me_5)Me_4 as the reducing agent which proceeds via an "η^2-acetone" or oxytantallacyclopropane intermediate.

Ta(η^5-C_5Me_5)Me_4 (**1**)[6] reacts rapidly with 1 mol of CO at 25 °C to give (in 80% yield) an "η^2-acetone" complex,[7] monomeric **2** (eq 1).[10a] Its IR spectrum shows a peak at 1200 cm^{-1} which we believe is ν_{C-O}; **2** therefore may be more accurately described as an oxytantallacyclopropane complex. Since its ^1H and ^{13}C NMR spectra[10b] show only three types of methyl groups (5:2:2 ratio) and since the peak for the acetone methyl group broadens significantly at −80 °C in tol-d_8 in the 270-MHz ^1H NMR spectrum, we suggest the molecule has a ground-state pseudo-tetragonal-pyramidal geometry which rearranges rapidly under most conditions. Acetone is produced on treating **2** with oxygen, but bound acetone does not exchange readily with free acetone-d_6. η^2-Acetone is reduced to 2-propanol (appropriately labeled using D_2O) on treating **2** with water; 2 mol of methane is also formed. The reaction of **1** with 94% ^{13}C-enriched CO (*CO) gave Ta(η^5-C_5Me_5)(O=*CMe_2)Me_2 (**2**-**C*).[11] The peak we suspect is ν_{C-O} in **2** (at 1200 cm^{-1}) shifts to 1180 cm^{-1} in **2**-**C*. We could detect no intermediate between **1** and **2** in low-temperature ^{13}C NMR experiments.



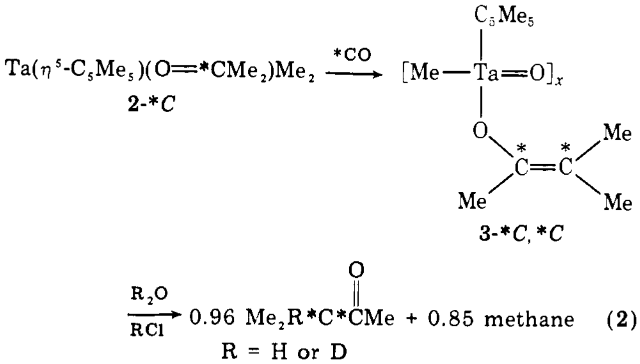
1

2

R = H or D

(1)

Ta(η^5-C_5Me_5)(acetone)Me_2 absorbs a second mole of CO more slowly at 25 °C to give another sublimable (180 °C, 1 μ) pale yellow complex (**3**,[12] 90% yield) whose ^1H and ^{13}C NMR spectra[13] suggest that five different methyl groups are present (5:1:1:1:1) and whose IR spectrum shows a medium strength band at 1670 cm^{-1}. Treating **2**-**C* with CO gave a product (**3**-**C,C*) in which the CO carbon atoms have not scrambled[14] and J_{C*C} = 88 Hz, consistent with a C(sp^2)-C(sp^2) coupling constant;[3,11b] the IR band shifts to 1640 cm^{-1}. Hydrolysis of **3**-**C*,**C* gives 1 mol of methane and 1 mol of appropriately labeled methyl isopropyl ketone-$^{13}C_2$ (eq 2). Therefore, we postulate that **3** contains an enolate ligand.[15] However, **3** is not a discrete monomer (mol wt 640 ± 40 in benzene; calcd 432) but, we believe, a mixture of linear or cyclic oligomers containing $-\!\left(\text{Ta-O-Ta-O}\right)\!-$ bonds. This is consistent with the fact that the region in which a metal-oxygen stretching frequency would be expected (1000-700 cm^{-1}) contains many relative weak peaks rather than a single strong peak, characteristic of (e.g.) $\nu_{Ta=O}$. We also know that **3** can be hydrolyzed with 1 equiv of ROH (R = Me or Me_3C) to give 1 equiv of methyl isopropyl ketone and pentane-soluble pale yellow products which are also inseparable mixtures of several complexes.



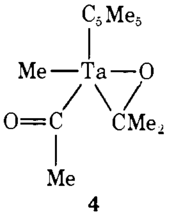
2-**C*

3-**C*,**C*

(2)

The reaction between a 1:1 mixture of Ta(η^5-C_5Me_5)(CH_3)$_4$ and Ta(η^5-C_5Me_5)(CD_3)$_4$ (pre-mixed at 25 °C) in ether at −78 °C with 2 mol of CO followed by hydrolysis gave only $(CH_3)_2HCC(O)CH_3$ and $(CD_3)_2HCC(O)CD_3$ (54% d_0, 1% d_3, 2% d_6, 43% d_9). This suggests that the methyl groups in **1**-d_0 and **1**-$(CD_3)_4$ do not scramble readily and **3** is formed entirely intramolecularly.

The two most reasonable intermediate products of the reaction of **2** with CO are **4** and **5**. In either the acyl may be best



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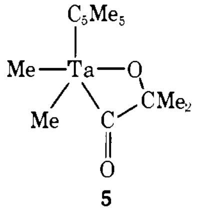

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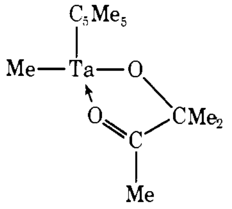

6

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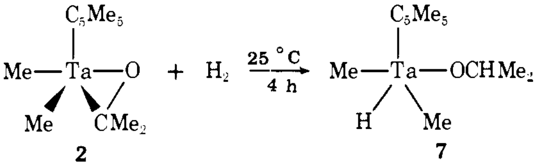
described as an oxycarbene ligand[3] which couples to a methyl (in **5**) or acetone carbon atom (in **4**) to give **6**, which then rearranges to **3**. If **4** is an intermediate, the coupling reaction must be rather specific and $Ta(\eta^5\text{-}C_5Me_5)(\eta^2\text{-acetone})_2$ cannot form reversibly to any significant extent.

The course of the reaction of **2** with H_2 may prove relevant to the question of whether **4** or **5** is formed. At 25 °C in benzene under 40 psi of H_2, **2** smoothly and quantitatively is converted into **7** in 4 h (eq 3).[17] The fact that no methane is formed suggests that the Ta-C (acetone) bond is more readily cleaved by H_2. Therefore, it may also react more rapidly with CO to give **5** rather than **4**. We have not yet isolated **7** since it decomposes (apparently bimolecular) in solutions more concentrated than ~0.02 M[18] to give methane and unidentified organometallic products.



$$Me{-}\overset{C_5Me_5}{\underset{Me\quad CMe_2}{Ta}}{-}O + H_2 \xrightarrow[4\ h]{25\ ^\circ C} Me{-}\overset{C_5Me_5}{\underset{H\quad Me}{Ta}}{-}OCHMe_2 \qquad (3)$$

2 **7**

This model study suggests that reductive coupling of CO with H_2 to give two carbon products might plausibly proceed via CO insertion into the metal-carbon bond of an η^2-formaldehyde ligand[9] or by coupling a formyl and an η^2-formaldehyde ligand. We are attempting to prepare η^2-formaldehyde analogues of **2** in order to see if such expectations are realistic.

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(6) This pentane-soluble, sublimable, yellow complex can be prepared straightforwardly from $Ta(\eta^5\text{-}C_5Me_5)Me_3Cl$ and LiMe or MeMgX in ether. $Ta(\eta^5\text{-}C_5Me_5)Me_3Cl$ is prepared from $TaMe_3Cl_2$ and LiC_5Me_5 in ether. Cf. $Ta(\eta^5\text{-}C_5H_5)Me_3Cl$: Schrock, R. R.; Sharp, P. R. *J. Am. Chem. Soc.* **1978,** *100*, 2389–2399.

(7) The reaction of CO with several transition metal alkyl complexes is known to yield ketones,[8] but in no such case so far has an η^2-ketone complex been observed. However, a stable η^2-formaldehyde complex has now been prepared from $Os(CO)_2(PPh_3)_3$ and formaldehyde.[9]

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(10) (a) Calcd for $TaC_{15}H_{27}O$: C, 44.56; H, 6.72; mol wt, 404 (in cyclohexane). Found: C, 43.93; H, 6.79; mol wt, 412. It sublimes at 60–90 °C and 0.1-μ without change. (b) ^1H NMR (τ, tol-d_8): 8.17 (s, 6, Me_2CO), 8.34 (s, 15, C_5Me_5), 9.93 (s, 6, TaMe). ^{13}C NMR (ppm, C_6D_6, ^1H gated decoupled): 115 (s, C_5Me_5), 111 (s, $Me_2\mathit{C}O$), 55.6 (q, TaMe, $^1J_{CH}$ = 119 Hz), 28.1 (q, Me_2CO, $^1J_{CH}$ = 122 Hz), 10.7 (q, $C_5\mathit{Me}_5$, $^1J_{CH}$ = 127 Hz).

(11) (a) The acetone methyl peak in the ^{13}C NMR spectrum of **2**-*C is a doublet with $J_{C\cdot C}$ = 39 Hz, a typical[11b] $C(sp^3)$–$C(sp^3)$ coupling constant. (b) Axenrod, T.; Webb, G. A. "Nuclear Magnetic Resonance Spectroscopy of Nuclei other than Protons"; Wiley: New York, 1974; p 187–218.

(12) Analyses of air- and moisture-sensitive compounds are characteristically low (see the results for **2**[10a]). We think that, because **3** is especially sensitive to water, analyses have been less successful than normal. Calcd for $TaC_{16}H_{27}O_2$: C, 44.45; H, 6.29. Found: C, 43.67; H, 6.01.

(13) ^1H NMR (τ, $CDCl_3$): 8.04 (s, 15, C_5Me_5), 8.35, 8.37, 8.50 (s, 3 each, methyl groups on enolate ligand), 9.85 (s, 3, TaMe). ^{13}C NMR (ppm, $CDCl_3$, ^1H gated decoupled): 149 (s, $OMe\mathit{C}{=}CMe_2$), 119 (s, C_5Me_5), 102 (s, $OMeC{=}\mathit{C}Me_2$), 37.1 (q, TaMe, $^1J_{CH}$ = 121 Hz), 19.1, 17.7, 17.5 (q, methyl groups on enolate ligand, $^1J_{CH}$ = 126 Hz), 10.5 (q, $C_5\mathit{Me}_5$, $^1J_{CH}$ = 128 Hz).

(14) The ^1H NMR spectrum of **3**-*C,C shows that the peaks at 8.35 and 8.50 are due to $O(Me)C{=}{}^*C\mathit{Me}_2$ ($^2J_{H\cdot C}$ = 6 Hz). In the ^{13}C NMR spectrum the peaks at 19.1 and 17.7 are associated with these methyl groups ($J_{C\cdot C}$ = 43 Hz and 44 Hz, respectively). The peak at 102 is due to $O(Me)C{=}{}^*\mathit{C}Me_2$ and that at 149 to $O(Me)\mathit{C}{=}{}^*CMe_2$ with $^1J_{C\cdot C}$ = 88 Hz.

(15) Enolate ligands bound to Ta are produced with $Ta(CH_2CMe_3)_3(CHCMe_3)$ reacts with acyl chlorides.[16] The IR and ^1H NMR characteristics and hydrolysis products parallel those found for **3**.

(16) Schrock, R. R.; Fellmann, J. D. *J. Am. Chem. Soc.* **1978,** *100*, 3559–3568.

(17) ^1H NMR (τ, C_6D_6): 5.41 (sept, 1, $OC\mathit{H}Me_2$ $^3J_{HH}$ = 6 Hz), 7.97 (s, 15, C_5Me_5), 8.72 (d, 6, $OCH\mathit{Me}_2$, $^3J_{HH}$ = 6 Hz), 9.15 (d, 6, TaMe, $^3J_{HH}$ = 3 Hz). The hydride peak has not yet been located. IR (solution): $\nu_{Ta\text{-}H}$ 1730 cm^{-1}. (These assignments were confirmed by preparing **7** with D_2.[18]) The trans configuration shown in eq 3 is arbitrary.

(18) Rocklage, S., unpublished results.

(19) Camille and Henry Dreyfus Teacher–Scholar Grant Recipient, 1978.

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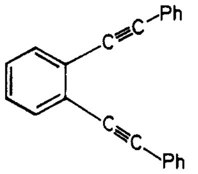
Coupling of Acetylenes Held Proximate to a Metal: Alkyne–Alkyne Interactions in *cis*-Phosphinoacetylene Complexes

Sir:

Unusual chemical reactivity, particularly toward inter- and intramolecular coupling, is often associated with aromatic diacetylenes such as **1** in which the two alkynyl groups are held rigidly adjacent to one another.[1,2] During our studies on the synthetic utility of coordinated heteroatom functionalized acetylenes,[3] we discovered a novel method to achieve the proximity of alkyne triple bonds necessary to promote coupling. Thus in cis transition metal complexes of phosphorus coordinated alkynyl phosphines, for example **2** (M = Pd, Pt; X = Cl; R = R′ = Ph), the sterically less demanding -C≡CR′ groups are forced into a configuration facilitating alkyne–alkyne interaction. We have established the nature of these unusual alkyne–alkyne contacts via a single-crystal X-ray analysis of



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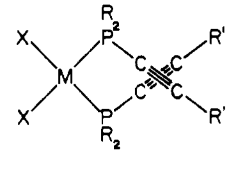

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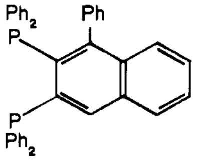

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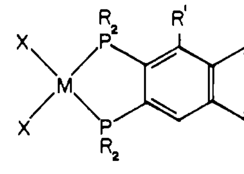

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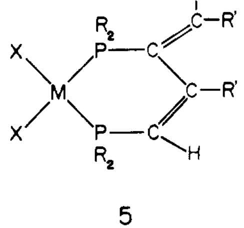

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