bifurcation.[7] This behavior, illustrated in Figure 3, resembles but is not identical with the subcritical Hopf bifurcation and resulting bistability between a stationary and an oscillatory state found in the chlorite–iodide system.[5]

If the iodide and bromate input concentrations are increased still further, we reach a critical point P at which the two stationary states simultaneously become unstable. Beyond this point, the oscillatory state is the only stable one. This region of oscillatory monostability widens, in accordance with the cross-shaped diagram model,[5,8] as the input concentrations are increased. Quantitative measurements in this range are hampered, however, by significant iodine precipitation.

While the mechanism for this system remains to be worked out, two different schemes can be envisioned that would lead to oscillation. Iodide could reduce enough bromate to bromide to provide a source of that essential species, while simultaneously generating the 1-equiv redox couple required for the autocatalytic production of $HBrO_2$, which drives the key process in the mechanisms of other bromate oscillators.[3] Some higher oxidation states of iodine such as I, HIO, IO, HIO_2, or IO_2 would presumably play the important role of the redox couple.

Alternatively one may invoke a mechanism similar to that of the chlorite–iodide oscillating system. Preliminary work suggests that such a mechanism will involve a key binuclear intermediate $IClO_2$ in the ClO_2^-–I^- reaction and probably $IBrO_2$ in the present one.

It is somewhat surprising that earlier rate studies of the iodide–bromate reaction in a closed system give no indication of autocatalytic or even complex kinetics. Barton and collaborators[9,10] obtain a rate law

$$\frac{-d[BrO_3^-]}{dt} = k[H^+]^2[BrO_3^-][I^-] \qquad (1)$$

with a stoichiometry

$$BrO_3^- + 9I^- + 6H^+ \rightarrow Br^- + 3I_3^- + 3H_2O \qquad (2)$$

Since all other homogeneous oscillators discovered thus far involve some form of autocatalysis, it seems worth reinvestigating reaction 2, especially in view of a reported induction period[11] before it proceeds. The iodine–bromate reaction, which proceeds through a series of intermediates,[12] also appears to merit further study in this connection.

The iodide–bromate reaction can be augumented by the addition of a flow of Mn^{2+} to give a system that has two different oscillatory and three different stationary states. Details of this and related bromate oscillators will appear in a forthcoming publication.

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Registry No. BrO_3^-, 15541-45-4; I^-, 20461-54-5.

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Reduction of Carbon Monoxide by Binuclear Tantalum Hydride Complexes

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Abstract: $[TaCp'Cl_2H]_2$ ($Cp' = \eta^5\text{-}C_5Me_4Et$) reacts with CO to give yellow, crystalline $Ta_2Cp'_2Cl_4(H)(CHO)$; the hydride bridges the two metals as does the side-on bonded formyl fragment. When PMe_3 is added to $Ta_2Cp'_2Cl_4(H)(CHO)$ the formyl C–O bond is broken to give $Ta_2Cp'_2Cl_4(H)(O)(CHPMe_3)$. The reaction of a mixture of $[TaCp'Cl_2H]_2$ and $[TaCp'Cl_2D]_2$ with CO followed by PMe_3 to give only a mixture of $Ta_2Cp'_2Cl_4(H)(O)(CHPMe_3)$ and $Ta_2Cp'_2Cl_4(D)(O)(CDPMe_3)$ suggests that the dimer does not fragment when it reacts with CO. This was confirmed by a crossover experiment involving $[TaCp'Cl_2H]_2$ and $[TaCp^sCl_2H]_2$ ($Cp^s = \eta^5\text{-}1,3\text{-}C_5H_3(SiMe_3)_2$). $[TaCp'Cl_2H]_2$ forms a green, diamagnetic pyridine adduct that contains two inequivalent hydride ligands. $[TaCp'Cl_2H]_2$ forms an unstable, purple CO adduct that shows a terminally bound CO band ($\nu_{CO} = 1939$ cm^{-1}) and two different hydride bands ($\nu_{MH} = 1560$ and 1599 cm^{-1}) in the IR spectrum of a thin film at −78 °C, and a singlet ascribed to the carbonyl carbon atom at 238 ppm in the ^{13}C NMR spectrum. $[TaCp'Cl_2H]_2(CO)$ decomposes rapidly in solution or in the solid state at −30 °C to give $Ta_2Cp'_2Cl_4(H)(CHO)$ quantitatively. Methane is formed in ~70% yield when $Ta_2Cp'_2Cl_4(H)(CHO)$ is treated with $AlCl_3$ under molecular hydrogen. Methanol is formed in high yield when $Ta_2Cp'_2Cl_4(H)(CHO)$ is hydrolyzed with aqueous HCl.

There is a lively interest in the selective reduction of carbon monoxide to a product containing two or more carbon atoms.[1] It is thought that such selectivity is more likely with a homogeneous catalyst, and that the reduction product will likely still contain at least one oxygen atom.[2] The best example so far of some degree of selectivity to a two-carbon product is the Rh-catalyzed reduction of CO to ethylene glycol.[2g]

Although there have been many elegant studies of the chemistry of formyl complexes and other likely intermediates in systems in

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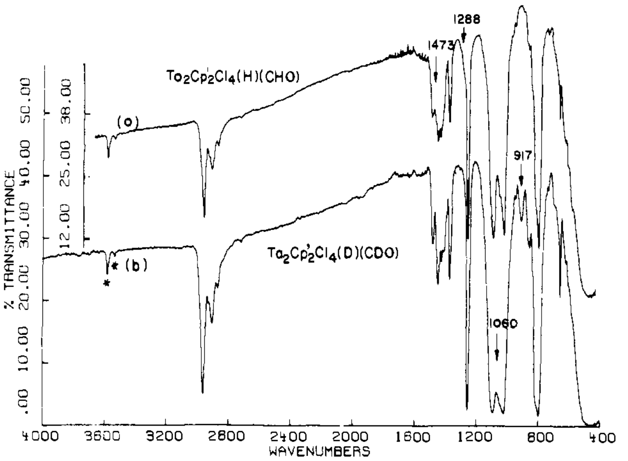

Figure 1. FT IR spectra of (a) $Ta_2(Cp')_2Cl_4(H)(CHO)$ and (b) $Ta_2(Cp')_2Cl_4(D)(CDO)$ at -78 °C (thin films on NaCl; see Experimental Section; (*) traces of water in or on the NaCl windows).

which CO is reduced,[3] several important questions have not been answered. One of the most important is whether one metal center is sufficient for the formation of an intermediate formyl complex that is long-lived and reactive enough to be reduced further, or whether one or more additional metal centers must be present in order to stabilize the formyl ligand by interacting with its oxygen atom. (We need not at this point specify whether the metals are constrained in a metal cluster or a dimer or are simply reacting in a bimolecular fashion.) Model studies point to the latter as at least a potentially important feature of CO reduction.[4,5] However, it must also be noted that there are now two examples of formation of a mononuclear formyl complex from a metal hydride complex and carbon monoxide.[6]

The most dramatic example of the role a second metal might play is addition of a zirconium hydride to a carbonyl ligand bound to another metal to give "zirconoxycarbene" complexes, e.g., $(\eta^5\text{-}C_5Me_5)_2Zr(H)[O(H)C{=}W(\eta^5\text{-}C_5H_5)_2]$.[5a] The "carbene-type" CHO ligand is potentially an important type of "stabilized formyl" complex. Reactions between $Zr(\eta^5\text{-}C_5Me_5)_2H_2$ and CO may involve similar but as yet unobserved intermediates.[5b]

A problem that almost certainly will be insurmountable as far as a zirconium-based catalytic CO reduction system is concerned is the strength of the zirconium-oxygen bond. An important question is then what other metal-hydride complexes will reduce carbon monoxide but can still be regenerated by reaction of an intermediate with molecular hydrogen? Our approach is to systematically decrease the "oxophilicity" of the metal by moving to the right of group 4, first to group 5 metals. However, since known niobium and tantalum hydride complexes simply form hydrido carbonyl complexes in the presence of carbon monoxide,[7] we first had to prepare a new type of tantalum hydride complex, $[Ta(\eta^5\text{-}C_5Me_4R)Cl_2H]_2$ (R = Me or Et).[8] $[Ta(\eta^5\text{-}C_5Me_4R)Cl_2H]_2$ does indeed reduce carbon monoxide to give a dimeric formyl hydride complex in high yield. This reduction, the formation of an unstable CO adduct of the parent hydride complex, and the formation of methane and methanol from the formyl hydride complex are the results we will discuss in this paper. A few of these results have been reported in a preliminary communication.[9]

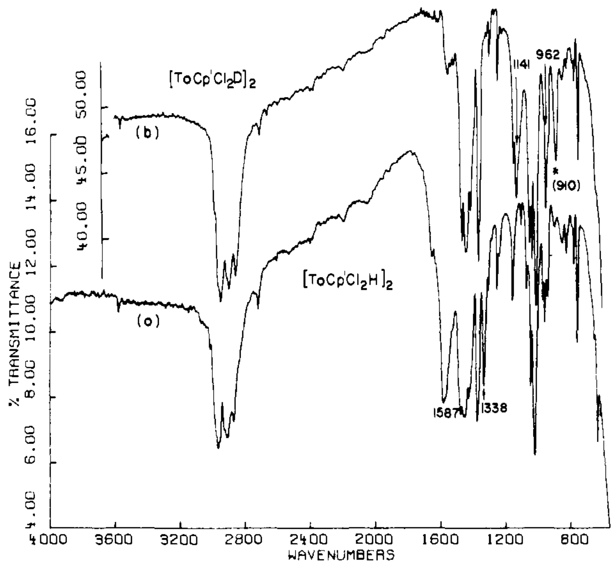

Figure 2. FT IR spectra of (a) $[Ta(Cp')Cl_2H]_2$ and (b) $[Ta(Cp')Cl_2D]_2$ at -78 °C (thin film on NaCl; (*) an irreproducible peak believed to be due to a Ta-O mode in traces of an oxide impurity).

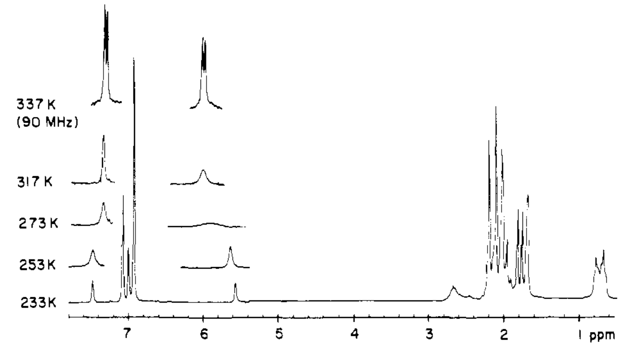

Figure 3. Variable-temperature ^1H NMR spectrum of $Ta_2(\eta^5\text{-}C_5Me_4Et)_2Cl_4(H)(CHO)$ in toluene-d_8 (*) at 250 MHz (except $T = 337$ K).

Results

Preparation and Properties of $Ta_2(\eta^5\text{-}C_5Me_4R)_2Cl_4(H)(CHO)$. $[TaCp'Cl_2H]_2$ ($Cp' = \eta^5\text{-}C_5Me_4Et$) reacts within 10 min at 0 °C with 1 equiv of carbon monoxide (rapidly with an excess at ~1 atm) to give yellow, crystalline $Ta_2Cp'_2Cl_4(H)(CHO)$. $Ta_2Cp'_2Cl_4(H)(CHO)$ is soluble in THF, chlorocarbons, and aromatic hydrocarbons, sparingly soluble in diethyl ether, and insoluble in pentane. $Ta_2Cp'_2Cl_4(D)(CDO)$ and $Ta_2Cp'_2Cl_4(H)(^{13}CHO)$ were prepared similarly. $Ta_2Cp''_2Cl_4(H)(CHO)$ ($Cp'' = \eta^5\text{-}C_5Me_5$) can be prepared straightforwardly, but since it is only sparingly soluble in aromatic hydrocarbons it is less convenient to manipulate than $Ta_2Cp'_2Cl_4(H)(CHO)$.

The -78 °C FT IR spectra of $Ta_2Cp'_2Cl_4(H)(CHO)$ and $Ta_2Cp'_2Cl_4(D)(CDO)$ as thin films on a sodium chloride window (see Experimental Section) are shown in Figure 1. In contrast to the relatively straightforward -78 °C FT IR spectra of $[TaCp'Cl_2H]_2$ and $[TaCp'Cl_2D]_2$, which show two peaks ascribable to $Ta_2(\mu\text{-}H)_2$ modes (Figure 2),[10] there are no obvious tan-

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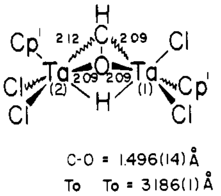

Figure 4. Schematic drawing of the structure of $Ta_2(\eta^5\text{-}C_5Me_4Et)_2Cl_4(H)(CHO)$.

talum–hydride or tantalum–deuteride bands. The shoulder at 1288 cm^{-1} (Figure 1a) and the small peak at 917 cm^{-1} are reproducible, and the ratio of their frequencies is 1.40. Therefore, in spite of the fact that the 917 cm^{-1} is uncomfortably close to the position of a peak at 910 cm^{-1} that is most likely due to an oxide impurity (Figure 2b), we believe that 1288 cm^{-1} is the approximate location of a metal–hydride band. It is possible that the intensity at 1473 cm^{-1} in the spectrum of $Ta_2Cp'_2Cl_4(H)(CHO)$ (1060 cm^{-1} in the spectrum of $Ta_2Cp'_2Cl_4(D)(CDO)$) is another, higher energy Ta–H band, but we by no means can be certain.

The ^1H NMR spectrum of $Ta_2Cp'_2Cl_4(H)(CHO)$ at 233 K (Figure 3) suggests that the molecule has no symmetry. The 5.6 and 7.5 ppm peaks in the ^1H NMR spectrum of $Ta_2Cp'_2Cl_4(H)(^{13}CHO)$ are split into doublets with J_{CH} = 20 and 168 Hz, respectively. Therefore, the two singlets at ca. 5.6 and 7.5 ppm can be assigned to the hydride and formyl protons, respectively. In the ^{13}C NMR spectrum of $Ta_2Cp'_2Cl_4(H)(^{13}CHO)$ between 250 and 300 K the formyl carbon atom resonance is a broad doublet (J_{CH} = 168 Hz) at 168 ppm. The 20-Hz coupling of the ^{13}C formyl carbon atom to the hydride could not be resolved.

A complicating feature of the ^1H NMR spectrum of $Ta_2Cp'_2Cl_4(H)(CHO)$ is its temperature dependence (Figure 3). As the temperature is raised from 233 to 337 K, the formyl and hydride signals broaden, shift toward one another, and sharpen into doublets with $J_{HH} \approx 4$ Hz. The resonances due to the Cp′ ligands shift somewhat, but the molecule remains asymmetric. In the ^{13}C NMR spectrum the resonance of the formyl carbon atom shifts from ~168 to ~176 ppm and the coupling between the formyl carbon atom and the formyl proton drops from ~175 to 165 Hz over this temperature range. However, the signal remains relatively broad. One could ascribe the changes in the ^1H NMR spectrum to ordinary temperature-dependent chemical shifts if the formyl proton resonance did not collapse to the extent it does at ca. 273 K. The only explanation we feel comfortable with is that one structural form of $Ta_2Cp'_2Cl_4(H)(CHO)$ predominates at low temperatures,but at high temperatures there is a significant amount of a second species present with which the first species interconverts rapidly. (Note that the hydride and formyl protons do not exchange on the NMR time scale during this process.) This postulate seems reasonable since we will see later that two isomers of $Ta_2[\eta^5\text{-}1,3\text{-}C_5H_3(SiMe_3)_2]_2Cl_4(H)(CHO)$ are observed in a 1:1 ratio. We should point out that the inequivalent hydride ligands in $Ta_2Cp'_2Cl_3H_2(R)$ complexes exchange at a rate of the order of the NMR time scale over the same temperature range, also without destroying the asymmetry of the molecule.[8] The temperature-dependent process in $Ta_2Cp'_2Cl_4(H)(CHO)$ could involve a structural change related to that occurring in $Ta_2Cp'_2Cl_3H_2(R)$. Also note that in a structurally related molecule, $Ta_2Cp'_2Cl_4(H)(O)(CHPMe_3)$ (see later), coupling between what were the two initial hydride ligands can be resolved, and it is of the same magnitude as that found in $Ta_2Cp'_2Cl_4(H)(CHO)$ at 337 K.

Churchill and Wasserman have determined the structure of $Ta_2Cp'_2Cl_4(H)(CHO)$.[11] We will briefly summarize their findings here. A schematic drawing of $Ta_2Cp'_2Cl_4(H)(CHO)$ is shown in Figure 4. The hydride and formyl ligands bridge between two skewed $TaCp'Cl_2$ fragments. Neither the hydride nor the formyl proton was located, although a hole for the bridging hydride is present in a position trans to the Cp′ group bound to Ta(2) such that the Ta(C)(O)(H)Ta core of this molecule approximates a trigonal bipyramid. The formyl proton must be terminally bound to the formyl carbon atom, since if it were bridging a Ta–C edge of the Ta(C)(O)(H)Ta core, J_{CH} would almost certainly be about half (or even less than half) what it is (168 Hz).[3h,12] The Ta---Ta distance (3.186 (1) Å) is too long for there to be a full Ta–Ta single bond between the two metals (cf. $[TaCp'Cl_2H]_2$[8]), although it is too short to propose that there is no significant interaction at all between the two metals. Note that the C–O bond is significantly longer (by ca. 0.02 Å) than one would expect to find in a typical alcohol or ether, and that the formyl fragment is essentially symmetrically bound between Ta(1) and Ta(2). There is no readily apparent steric reason why the mystery isomer proposed above could not be one in which the formyl ligand is rotated 180° (CH "trans" to Cp′ on Ta(1) instead of O "trans" to Cp′ on Ta(1)).

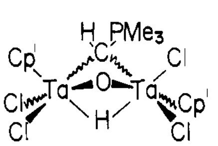

Figure 5. Schematic drawing of the structure of $Ta_2(\eta^5\text{-}C_5Me_4Et)_2Cl_4(H)(O)(CHPMe_3)$.

An alkyl derivative of the formyl hydride complex, $Ta_2Cp'_2Cl_3(H)(CHO)(CH_2SiMe_3)$, can be prepared in poor yield (17%) by reacting $Ta_2Cp'_2Cl_4(H)(CHO)$ with $Mg(CH_2SiMe_3)_2(dioxane)$. Its NMR spectra are similar to those of $Ta_2Cp'_2Cl_4(H)(CHO)$ (H*C*O at 167.4 ppm, *H*CO at 5.23 ppm, TaH at 7.26 ppm). The methylene protons of the CH_2SiMe_3 group are diastereotopic, as they are in $Ta_2Cp'_2Cl_3H_2(CH_2SiMe_3)$.[8] $Ta_2Cp'_2Cl_3(H)(CHO)(CH_2SiMe_3)$ could not be prepared from $Ta_2Cp'_2Cl_3H_2(CH_2SiMe_3)$ and CO.

$Ta_2Cp'_2Cl_4(H)(CHO)$ decomposes readily at ca. 80 °C in solution to a complex mixture of products, as judged by the ^{13}C NMR spectrum of a decomposed sample of $Ta_2Cp'_2Cl_4(H)(^{13}CHO)$. $Ta_2Cp'_2Cl_4(H)(CHO)$ does not react readily with 1 atm of molecular hydrogen or carbon monoxide at 25 °C. At higher temperatures and pressures (up to 1000 psi) complex mixtures of products are formed, some of which are unstable in the absence of CO and/or H_2, and none of which have yet been identified.

The Reaction of $Ta_2(Cp')_2Cl_4(H)(CHO)$ with PMe_3 and Evidence That Hydrides Do Not Scramble Intermolecularly When $[TaCp'Cl_2H]_2$ Reacts with CO. $Ta_2Cp'_2Cl_4(H)(CHO)$ reacts with PMe_3 in 30 min at 25 °C to give $Ta_2Cp'_2Cl_4(H)(O)(CHPMe_3)$ quantitatively. This product is soluble in aromatic hydrocarbons and diethyl ether, and it is stable in chlorocarbons. $Ta_2Cp'_2Cl_4(D)(O)(CDPMe_3)$ and $Ta_2Cp'_2Cl_4(H)(O)(^{13}CHPMe_3)$ can be prepared straightforwardly.

The structure of $Ta_2Cp'_2Cl_4(H)(O)(CHPMe_3)$[13] is shown schematically in Figure 5. Overall the structure resembles that of $Ta_2Cp'_2Cl_4(H)(CHO)$. The most important features are that PMe_3 has attacked the formyl carbon atom and that the C–O bond has been broken. The two metals therefore are pulled closer together (Ta---Ta = 2.992 (1) Å) than they are in $Ta_2Cp'_2Cl_4(H)(CHO)$, close enough to propose that a Ta–Ta bond is present. The hydride ligand again could not be located, although there is an obvious hole between the two metals where it should be (trans to one of the Cp′ ligands).

The ^1H NMR spectrum of $Ta_2Cp'_2Cl_4(H)(O)(CHPMe_3)$ is shown in Figure 6a. The hydride resonance at 9.84 ppm is a double doublet due to coupling to the ylide proton (5 Hz) and to phosphorus (2 Hz). The ylide proton resonance at 1.44 ppm shows a larger J_{HP} (13 Hz). The ylide proton signal in the

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[10] The Nujol mull spectra of $[Ta(Cp')Cl_2H]_2$ and $[Ta(Cp')Cl_2D]_2$ at 25 °C are qualitatively similar to those obtained at −78 °C.

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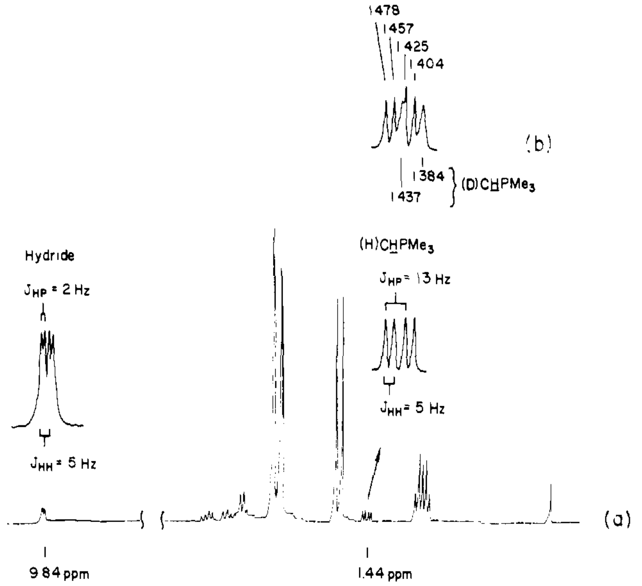

Figure 6. Hydride and ylide proton signals in the 250-MHz ^1H NMR spectrum of (a) $Ta_2(\eta^5\text{-}C_5Me_4Et)_2Cl_4(H)(O)(CHPMe_3)$; (b) $Ta_2(\eta^5\text{-}C_5Me_4Et)_2Cl_4(R)(O)(CR'PMe_3)$ (R, R' = H or D).

analogous spectrum of a product prepared from an approximate 1:2:1 mixture[8] of $Ta_2Cp'Cl_4H_2$, $Ta_2Cp'_2Cl_4(H)(D)$, and $Ta_2Cp'_2Cl_4D_2$ is shown in Figure 6b. The broad doublet due to the ylide proton in $Ta_2Cp'_2Cl_4(D)(O)(CHPMe_3)$ is found slightly further upfield of the double doublet for the ylide proton in $Ta_2Cp'_2Cl_4(H)(O)(CHPMe_3)$ as a result of the normal deuterium isotope effect. The hydride signal for the mixture of $Ta_2Cp'_2Cl_4(H)(O)(CDPMe_3)$ and $Ta_2Cp'_2Cl_4(H)(O)(CHPMe_3)$ is virtually the same pattern as that in Figure 6a except the right half of the double doublet pattern is more intense as a result of the contribution by $Ta_2Cl'_2Cl_4(H)(O)(CDPMe_3)$; the hydride signal therefore cannot be used to accurately detect the amount of $Ta_2Cp'_2Cl_4(H)(O)(CDPMe_3)$.

The fact that we can detect $TaCp'_2Cl_4(D)(O)(CHPMe_3)$ in the presence of $Ta_2Cp'_2Cl_4(H)(O)(CHPMe_3)$ by observing the ylide proton signal at 1.44 ppm allowed us to do the following experiment. A mixture of equal parts of $Ta_2Cp'_2Cl_4H_2$ and $Ta_2Cp'_2Cl_4D_2$ was treated first with CO and then with PMe_3. (Note that it was necessary to mix $[TaCp'Cl_2H]_2$ and $[TaCp'Cl_2D]_2$ at low temperature in order to avoid slow formation of $Ta_2Cp'_2Cl_4(H)(D)$.[8]) The recrystallized final product had an ^1H NMR spectrum essentially identical with that shown in Figure 6a; therefore we can say with certainty that <10% $Ta_2Cp'_2Cl_4(D)(O)(CHPMe_3)$ was present (eq 1). At first glance this result

$$Ta_2Cp'_2Cl_4H_2 + Ta_2Cp'_2Cl_4D_2 \xrightarrow[\text{2. }PMe_3]{\text{1. CO}} \begin{array}{r} Ta_2Cp'_2Cl_4(R)(O)(CR'PMe_3) \quad (1) \\ R = R' = H \text{ or } R = R' = D \end{array}$$

might appear to prove that the dimers do not break into monomers when they react with CO. However, it only proves that *if* they do, both hydrides (or deuterides) remain on one metal, and H and D do not scramble between H- or D-containing monomers before they react with CO (probably bound to the metal in the other monomer) to give the final product.

Experiments Involving η^5-1,3-$C_5H_3(SiMe_3)_2$ Complexes. Proof That the Hydride Dimer Remains Intact. In order to prove that the hydride dimer remains intact when it reacts with carbon monoxide we had to devise a means of detecting a formyl hydride complex containing two different cyclopentadienyl ligands. Since mass spectroscopic studies were not feasible, and since we could find no other means of detecting the crossover product using η^5-C_5Me_5 and η^5-C_5Me_4Et complexes, we turned to complexes containing the η^5-1,3-$C_5H_3(SiMe_3)_2(Cp^s)$ ligand.[14] We not only proved what we had set out to prove, but we learned more about dimeric formyl hydride complexes in the process.

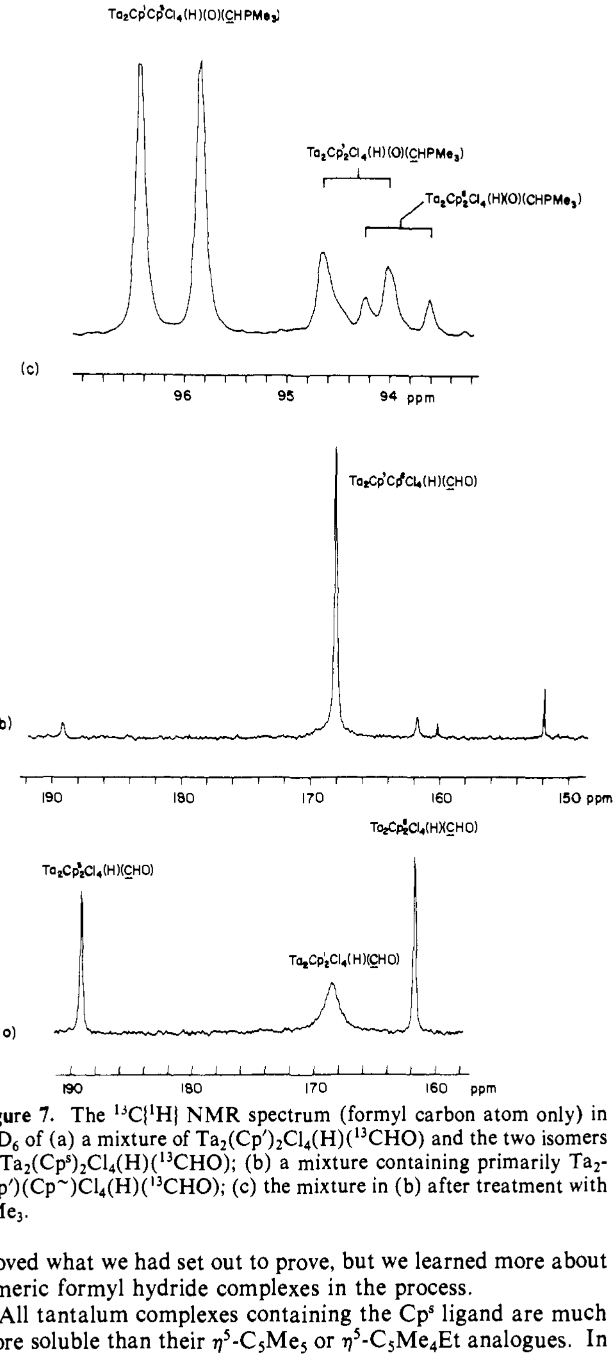

Figure 7. The $^{13}C\{^1H\}$ NMR spectrum (formyl carbon atom only) in C_6D_6 of (a) a mixture of $Ta_2(Cp')_2Cl_4(H)(^{13}CHO)$ and the two isomers of $Ta_2(Cp^s)_2Cl_4(H)(^{13}CHO)$; (b) a mixture containing primarily $Ta_2(Cp')(Cp^{\sim})Cl_4(H)(^{13}CHO)$; (c) the mixture in (b) after treatment with PMe_3.

All tantalum complexes containing the Cp^s ligand are much more soluble than their η^5-C_5Me_5 or η^5-C_5Me_4Et analogues. In fact, $TaCp^sCl_2$(propylene) is so soluble in pentane that it was not practical to isolate it. It was simply reacted in situ with molecular hydrogen to give green $[TaCp^sCl_2H]_2$. In order to avoid the tedious isolation of the formyl hydride complex, the system was further studied by ^{13}C NMR using ^{13}CO-labeled compounds.

$[TaCp^sCl_2H]_2$ reacts with ^{13}CO qualitatively more slowly at −78 °C in ether than $[TaCp'Cl_2H]_2$ does. A ^{13}C NMR spectrum of the product shows *two* equally intense, relatively sharp signals for formyl carbon atoms at 189.3 and 161.8 ppm (Figure 7a). In the gated spectrum they are doublets with J_{CH} = 185 and 177 Hz, respectively. Heating a sample to 80 °C causes it to decompose. At no point is there any evidence that the two isomers interconvert rapidly on the NMR time scale. Interestingly, this mixture of isomers reacts with PMe_3 to give a single $Ta_2Cp^s{}_2Cl_4(H)(O)(CHPMe_3)$ product with an ylide carbon signal at 93.8 ppm.

An approximately 1:1 mixture of $TaCp^sCl_2$(propylene) and $TaCp'Cl_2$(propylene) was treated with H_2. The resulting mixture of the three possible hydride dimers was largely the mixed species $Ta_2Cp'Cp^sCl_4H_2$ by ^1H NMR (see Experimental Section). This mixture reacts with ^{13}CO to give a mixture of the two isomers

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[14] Lappert, M. F.; Singh, A.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Chem. Commun.* **1981**, 1190.

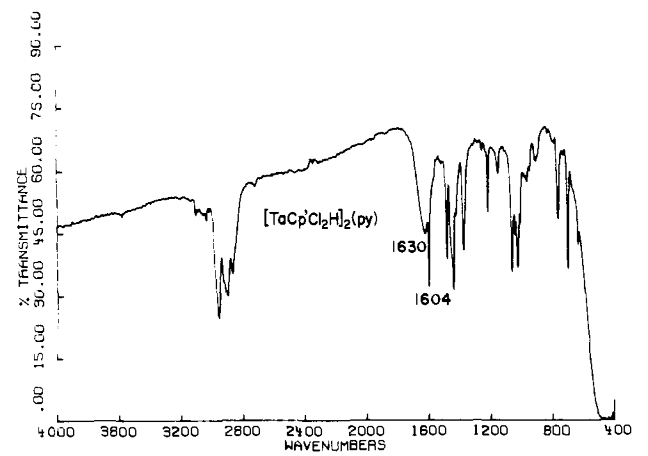


Figure 8. FT IR spectrum of $[Ta(Cp')Cl_2H]_2(py)$ at −78 °C (thin film on NaCl).

of $Ta_2Cp^s{}_2Cl_4(H)(CHO)$, $Ta_2Cp'_2Cl_4(H)(CHO)$, and at least three other formyl hydride species, but predominantly one "mixed" species with a resonance for the formyl carbon atom at 168.1 ppm (Figure 7b). Reaction of this mixture with PMe_3 produces a mixture of only three products in the ratio expected for a mixture of $Ta_2Cp^s{}_2Cl_4(H)(O)(CHPMe_3)$, $Ta_2Cp'_2Cl_4(H)(O)(CHPMe_3)$, and (predominantly) $Ta_2Cp'Cp^sCl_4(H)(O)(CHPMe_3)$ (Figure 7c). Again, it appears that any configurational isomers of a formyl complex are converted into a single μ-oxo μ-ylide isomer.

A mixture of $Ta_2Cp^s{}_2Cl_4H_2$ and $Ta_2Cp'_2Cl_4H_2$ was treated with ^{13}CO in diethyl ether under three different conditions. First, 1.5 equiv of ^{13}CO was added at 0 °C. Second, 10 equiv of ^{13}CO was added at 0 °C. Third, 1 equiv of ^{13}CO was added at −78 °C (to give the purple CO adduct described below) followed by removal of excess CO and warming the reaction to 25 °C. In all three cases only a mixture of $Ta_2Cp^s{}_2Cl_4(H)(CHO)$ and $Ta_2Cp'_2Cl_4(H)(CHO)$ was obtained, and after reaction with PMe_3, only a mixture of $Ta_2Cp^s{}_2Cl_4(H)(O)(CHPMe_3)$ and $Ta_2Cp'_2Cl_4(H)(O)(CHPMe_3)$ was obtained. Therefore, barring the unlikely possibility that the mixed species, $Ta_2Cp'Cp^sCl_4(H)(CHO)$, is energetically unfavorable, or that it forms especially slowly from monomeric units (while $Ta_2Cp'_2Cl_4(H)(CHO)$ and $Ta_2Cp^s{}_2Cl_4(H)(CHO)$ re-form selectively from monomers), we can confidently conclude that the dimeric hydride complexes do not break up into monomeric units of any type to any significantly extent when they react with carbon monoxide to give the formyl hydride complexes.

The Formation of Adducts between $[Ta(Cp')Cl_2H]_2$ and Pyridine or CO. $[Ta(Cp')Cl_2H]_2$ reacts with pyridine to form dark green needles of a diamagnetic, dimeric 1:1 adduct. The IR spectrum of $[TaCp'Cl_2H]_2(py)$ (Figure 8) shows a metal–hydride peak at 1630 cm^{-1} in addition to a sharp peak due to pyridine at 1604 cm^{-1}; in $[TaCp'Cl_2D]_2(py)$ the hydride peak is observed at 1165 cm^{-1}. In the NMR spectrum of $[TaCp'Cl_2H]_2(py)$ we see only one hydride resonance at 0.287 ppm, but in the spectrum of $[TaCp''Cl_2H]_2(py)$ in bromobenzene we see two hydride signals at 0.273 and 0.456 ppm. (In the spectrum of $[TaCp'Cl_2H]_2(py)$ the second hydride peak must be obscured by other resonances.) Since the two hydride resonance are so close to one another we assume the two inequivalent hydrides are either both bridging or both terminal. Although they almost certainly are still bridging it is peculiar that the signals are shifted to such a higher field than where they are found in the spectrum of the parent complex. Another unusual feature of the NMR spectrum of the pyridine adduct is that all five pyridine protons are different. This result suggests that the pyridine is bound to one of the two metals where it cannot rotate about the pyridine–Ta bond axis rapidly on the NMR time scale. $[TaCp'Cl_2H]_2(py)$ will still react with CO to give $[TaCp'Cl_2]_2(H)(CHO)$ but slowly (10 min, 25 °C, 1 atm) relative to the rate at which $[TaCp'Cl_2H]_2$ reacts with CO. It is reasonable to expect that pyridine must be lost from the adduct before it can react with CO.

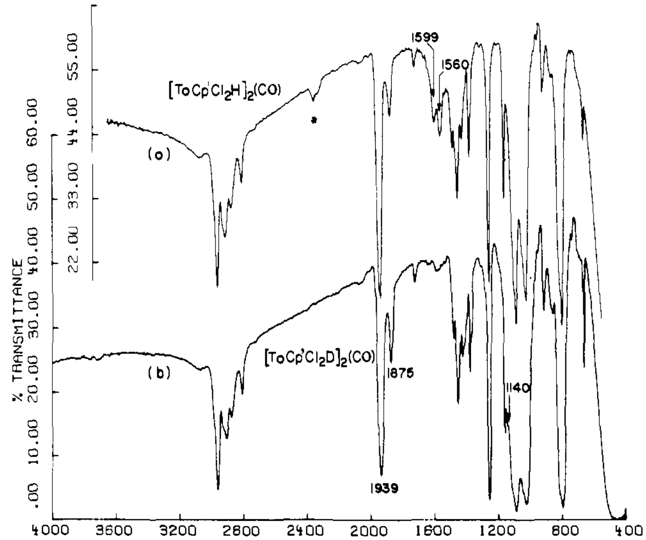


Figure 9. FT IR spectrum of (a) $[Ta(Cp')Cl_2H]_2(CO)$ and (b) $[Ta(Cp')Cl_2D]_2(CO)$ at −78 °C (thin film on NaCl; * residual CO_2 in sample compartment).

When a green solution of $[TaCp'Cl_2H]_2$ is treated with excess CO at −78 °C it turns deep purple. One equivalent of CO is sufficient although the rate of formation of $[TaCp'Cl_2H]_2(CO)$ is relatively slow under these conditions. Above −60 °C the purple solution turns green, and then yellow at −30 °C. $Ta_2Cp'_2Cl_4(H)(CHO)$, the only observable product, can be isolated quantitatively. We believe the color change from purple to green to yellow is only a consequence of the colors involved, not reversible loss of CO, since a thin film of $[TaCp'Cl_2H]_2(CO)$ on NaCl in vacuo is transformed into pure $Ta_2Cp'_2Cl_4(H)(CHO)$ over a period of 1 h at 25 °C. (However, no IR detectable $[TaCp'Cl_2H]_2(CO)$ forms at −78 °C from solid $[TaCp'Cl_2H]_2$ (thin film on NaCl) in an atmosphere of CO in 1 h.)

The −78 °C IR spectra of $[TaCp'Cl_2H]_2(CO)$ and $[TaCp'Cl_2D]_2(CO)$ as thin films on NaCl are shown in Figure 9. Two hydride peaks are found at 1599 and 1560 cm^{-1} and a terminal carbonyl peak at 1939 cm^{-1} in the IR spectrum of $[TaCp'Cl_2H]_2(CO)$. In the IR spectrum of $[TaCp'Cl_2D]_2(CO)$ (Figure 9b) the two hydride peaks shift to approximately 1140 cm^{-1} under one of the primary absorbances due to the Cp′ ligand. Note that the CO band (and its ^{13}CO shoulder) do not shift in the spectrum of $[TaCp'Cl_2D]_2(CO)$, suggesting that the modes that give rise to these absorptions are not mixed with hydride modes. The tiny peak at ca. 1725 cm^{-1} in the spectrum of $[TaCp'Cl_2H]_2(CO)$ and $[TaCp'Cl_2D]_2(CO)$ has not been identified, but at least it is not associated with a hydride ligand.

A sample of $[TaCp'Cl_2H]_2$ in toluene-d_8 was treated with 10 equiv of ^{13}CO at −78 °C for 2 days. A ^{13}C NMR spectrum at −78 °C showed two peaks in the low-field region. One was clearly due to $Ta_2Cp'_2Cl_4(H)(CHO)$. The second one was found at 238 ppm and showed no splitting (≲5 Hz) in the gated spectrum. The ratio of the two peaks was ~1:2 at −78 °C. Upon warming of the sample to 25 °C the 238 ppm peak disappeared. Thus, the 238 ppm peak must be ascribed to the carbonyl ligand in $[TaCp'Cl_2H]_2(CO)$.

Reaction of $Ta_2Cp'_2Cl_4(H)(CHO)$ with Lewis Acids To Give Methane. Aluminum trichloride reacts with $Ta_2Cp'_2Cl_4(H)(CHO)$ readily to give a complex mixture of unidentifiable products. Methane is produced in ~30% yield, but no ethylene or ethane. If $AlCl_3$ is added to $Ta_2Cp'_2Cl_4(H)(CHO)$ under 1 atm of excess H_2 the yield of methane rises to ~70% (eq 2). If

$$Ta_2Cp'_2Cl_4(H)(CHO) + AlCl_3 \xrightarrow{H_2\,(1\ \text{atm})} \sim 0.7CH_4 \quad (2)$$

D_2 is used, the methane consists of about a 2:3 mixture of CH_4 and CH_3D by ^{13}C NMR; the signal to noise ratio was not good enough to rule out up to 15% CH_2D_2. We propose that $AlCl_3$ attacks the formyl oxygen atom and causes the C–O bond to break.

The CH fragment is then reduced by the hydride in the same molecule or hydride ligands in other molecules. We cannot rule out the Cp groups as a source of H. However, it is clear that H_2 or D_2, even at 1 atm, can also help reduce the CH fragment at some point in the complex decomposition process.

Trimethylaluminum also reacts with $Ta_2Cp'_2Cl_4(H)(CHO)$. In the presence of 4 equiv of $AlMe_3$ the ^1H NMR spectrum of $Ta_2Cp'_2Cl_4(H)(CHO)$ shows a hydride resonance at 8.33 ppm and a formyl proton resonance at 6.5 ppm (J_{HH} = 3 Hz). *Two* carbon atom resonances ascribable to a formyl ligand are observed at 227 and 214 ppm, the first a broad doublet (J = 156 Hz), the second a double doublet (J = 153 and 9 Hz). This product can be isolated as a pentane-soluble yellow oil, which decomposes slowly at 25 °C to give methane (not quantified). If less than 3–4 equiv of $AlMe_3$ are added a more complex mixture of products is generated. Almost certainly the metals are being alkylated stepwise by $AlMe_3$. Since the methyl groups initially in $AlMe_3$ are likely sources of at least some of the methane, we did not study the formation and decomposition of the $AlMe_3$ product in detail.

$Ta_2Cp'_2Cl_4(H)(CHO)$ also reacts with $BH_3{\cdot}THF$ to yield a substantial quantity of methane (not quantified). Sodium borohydride (or borane–THF) has been used in several instances to reduce coordinated CO or a formyl ligand to a methyl ligand[3a–c,15a] or an acetyl to an ethyl ligand.[15b] In these cases, and in $Ta_2Cp'_2Cl_4(H)(CHO)$, initial attack by boron at the formyl oxygen atom is a likely first step.

The Reaction of $Ta_2Cp'_2Cl_4(H)(CHO)$ with HCl. Methanol (>80%) is produced when excess aqueous HCl is added to $Ta_2Cp'_2Cl_4(H)(CHO)$ in propanol (eq 3). If HCl gas is used

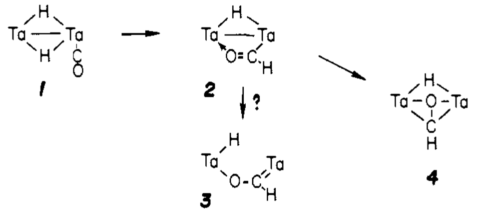
$$Ta_2Cp'_2Cl_4(H)(CHO) + HCl(aq) \xrightarrow{\text{propanol}} 0.80CH_3OH \quad (3)$$

in aprotic solvents no methanol is formed. Mixtures of yellow to orange products are obtained that show ^{13}C resonances characteristic of methoxide groups bound to tantalum (~60 ppm, J_{CH} ~ 145 Hz). These are most easily observed starting with $Ta_2Cp'_2Cl_4(H)(^{13}CHO)$. For example, the ^{13}C NMR spectrum of the product of the reaction of 2 equiv of HCl with $Ta_2Cp'_2Cl_4(H)(^{13}CHO)$ in bromobenzene showed two methoxide peaks, one at 66.84 ppm (major), the other at 62.85 ppm (minor). We believe, therefore, that the original C–O bond remains intact but the $Ta{-}OCH_3$ bond can only be cleaved by HCl in the presence of water or alcohol.

Discussion

When one finds a band that can be ascribed to a tantalum hydride mode at ca. 1600 cm^{-1}, it is not possible to say with any degree of certainty whether the hydride is terminal or bridging. For example, terminal Ta–H stretches are found at 1544 cm^{-1} in $TaH_5(dmpe)_2$,[7c] 1589 cm^{-1} in $Ta(H)(CO)_2(dmpe)_2$,[7c] 1750 cm^{-1} in $TaCp_2(H)(CO)$,[7a] and 1705 cm^{-1} in $TaCp_2(H)(PEt_3)$,[7a] to name a few. In contrast, the tantalum–(bridging hydride) band for $[TaCl_3(PMe_3)_2H]_2$, which has been structurally characterized,[16] occurs at 1260 cm^{-1}, as shown by deuterium labeling studies,[17] while the Ta–(bridging hydride) band in $[TaCp'Cl_2H]_2$ is found at 1587 cm^{-1}. The differences in energies of the Ta–(bridging hydride) modes in the two cases is actually not surprising since valence force field calculations for $[Mo_2(CO)_{10}(H)]^-$ show that the energies of the ν_3 modes can vary from ~1660 to ~1220 cm^{-1}, according to the Mo–H–Mo angle (180° to 90°, respectively).[18] Therefore, while we cannot say for certain that the hydride peaks observed in the IR spectra of $[TaCp'Cl_2H]_2(py)$ and $[TaCp'Cl_2H]_2(CO)$ are due to bridging hydrides, there is no good reason to propose otherwise. Most likely py or CO adds to one of the metals, thereby destroying the C_2 axis and yielding a complex with inequivalent hydride ligands (**1**, Scheme I).

Scheme I



Unfortunately, we have no clue as to how in detail the CO ligand is reduced. For example, it is possible that a *terminal* hydride (on the same *or* the other metal to which CO is bound) must be formed before it can transfer to carbon monoxide. But whatever the detailed mechanism, it would seem likely that the metal to which CO is *not* bound plays an important role, either as a hydride donor or as a Lewis acid interacting with the oxygen of the CO ligand or both. (For some time it has been proposed that "semibridging"[19] or "Lewis acid activated"[4] CO ligands should be more susceptible to reduction by a transition-metal hydride.) If a μ-H μ-formyl complex of type **2** were formed, it would most likely yield the observed "closed" structure, **4**, directly. Formation of the "tantaloxycarbene" tautomer, **3**, analogous to Bercaw's "zirconoxycarbene" complexes,[5] seems unnecessary as well as unlikely. It is unlikely since each metal in such a species would be electron deficient (14 electrons). It should be noted that if $Cp''_2(H)ZrO(H)C{=}WCp_2$ had a "closed" structure, tungsten would exceed its preferred 18-electron count and zirconium its preferred 16-electron count.

The formyl ligand is apparently stabilized by side-on bonding between the two metals, so much so that the formyl hydride complex will not react readily with CO to yield some species containing a C–C bond or with molecular hydrogen to give a methoxide ligand. However, sequestering the formyl ligand between two metals does not prevent what overall could be called an electrophilic or nucleophilic attack on it by acids and bases. As one might expect, a Lewis base (trimethylphosphine) attacks the formyl carbon atom and a Lewis acid (aluminum chloride) attacks the formyl oxygen atom. In each case the C–O bond is broken. Aluminum chloride is believed to act as an oxygen acceptor in a system in which CO is reduced by hydrogen to hydrocarbons with use of an iridium catalyst.[20] The precedent for nucleophilic attack on a formyl carbon atom is further reduction of formyl ligands by boron hydrides.[3a–c]

One of the remaining goals in this research is to discover what other ligands can be substituted for chlorides so that the ability of the hydride complex to reduce CO is retained, while at the same time the resulting formyl hydride complex becomes more reactive toward CO or more unstable with respect to transfer of the μ-hydride to the formyl carbon atom. With this approach we believe formation of a two-carbon CO reduction product under mild conditions will be possible.

Experimental Section

All operations, except where otherwise specified, were performed under dinitrogen either by Schlenk techniques or in a drybox. $[TaCp'Cl_2H]_2$, $TaCp'Cl_2(propylene)$, $[TaCp''Cl_2H]_2$,[8] and $1,3\text{-}C_5H_3(SiMe_3)_2$ anion[14] (Cp^s) were prepared as described in the literature.

Pentane, hexane, and petroleum ether were washed with 5% nitric acid in sulfuric acid, stored over calcium chloride, and distilled under dinitrogen from *n*-butyllithium. Reagent grade diethyl ether, tetrahydrofuran, and toluene were distilled from sodium benzophene ketyl under dinitrogen. Reagent grade benzene, methylene chloride, chloroform, and chlorobenzene were dried by refluxing overnight with calcium hydride

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and distilled. All deuterated NMR solvents had been passed through a column of activated alumina.

NMR data are listed in ppm relative to internal Me_4Si for ^1H and ^{13}C and relative to external H_3PO_4 for ^{31}P. The temperature is ca. 30 °C unless otherwise noted.

The infrared cell for low-temperature studies was a modification of that used for matrix isolation work.[21] The sodium chloride window, clamped in a copper block with indium gaskets, formed the base of a small reservoir (capacity ~6 mL). The copper block formed the base of a cold finger. Solutions could be introduced into the reservoir anaerobically and the solvent (e.g., dimethyl ether) pumped off at low temperature, leaving a thin film of material on the window.

Preparation of $Ta_2Cp'_2Cl_4(H)(CHO)$. $[TaCp'Cl_2H]_2$ (0.8 g, 1.0 mmol) was dissolved in 150 mL of diethyl ether in a 250-mL round-bottom flask. This was sealed with a septum cap and cooled to −78 °C. Carbon monoxide (25 mL, 1.1 mmol) was added by syringe through the septum and the reaction mixture was slowly warmed to 0 °C and stirred. The color of the solution changed from green to orange. After 2 days at 0 °C yellow needles (0.65 g, 78%) were filtered off. The filtrate was concentrated and cooled to −30 °C to give an additional 0.1 g (12%) as a yellow powder, which was pure by ^1H NMR: ^1H NMR (C_6D_6) δ 7.52 (br s, 1, MH), 5.73 (br s, 1, CHO), 2.71 (m, 4, $C_5CH_2CH_3$), 2.23 (br s, 6, C_5CH_3), 2.16 (br s, 6, C_5CH_3), 1.98 (br s, 3, C_5CH_3), 1.96 (br s, 3, C_5CH_3), 1.84 (br s, 6, C_5CH_3), 0.8 (m, 6, $C_5CH_2CH_3$); ^{13}C NMR (toluene-d_8, gated proton decoupled, 233 K) δ 11.3, 12.3, 12.4, 14.5, 15.1 (alkyl carbons), 168 (d, J_{CH} = 169 Hz, CHO); IR (Nujol) 1265 cm^{-1} (TaH, see Figure 1); M_r (cryoscopic in benzene) 832 (calcd), 800 ± 50 (found). Anal. Calcd for $Ta_2C_{23}H_{36}Cl_4O$: C, 33.19; H, 4.36. Found: C, 33.62; H, 4.40. In $Ta_2Cp'_2Cl_4(H)(^{13}CHO)$ (similarly prepared using Toepler pump techniques) the hydride resonance at 7.52 ppm is a doublet (J_{HC} = 20 Hz) and the formyl proton resonance at 6.08 ppm is a doublet (J_{HC} = 168 Hz).

Preparation of $Ta_2Cp'_2Cl_4(D)(CDO)$. $Ta_2Cp'_2Cl_4D(CDO)$ was prepared in the same manner from $[TaCp'Cl_2D]_2$ and carbon monoxide in diethyl ether: IR (Nujol) 920 cm^{-1} (TaD).

Preparation of $Ta_2Cp'_2Cl_3(H)(CHO)(CH_2SiMe_3)$. A toluene solution of $Ta_2Cp'_2Cl_4H(CHO)$ (0.42 g, 0.5 mmol) was cooled to −30 °C. $Mg(CH_2SiMe_3)_2$(dioxane) (0.07 g, 0.25 mmol) was added and the solution was stirred for 2 h at 25 °C. The solution was filtered and the solvent was removed in vacuo. The residue was dissolved in ether. Pentane was added and the solution was cooled to −30 °C to give orange crystals (0.15 g, 17%): ^1H NMR (C_6D_6) δ 7.37 (br s, 1, TaH), 5.27 (br s, 1, CHO), 1.6–3.0 (m, C_5CH_3), 1.4–0.8 (m, $C_5CH_2CH_3$), 0.27 (s, 9, $SiMe_3$); ^1H NMR (toluene-d_8, −30 °C) δ 7.26 (br s, 1, TaH), 5.23 (br s, 1, CHO), 3.43 (d, 1, J_{HH} = 12 Hz, $CH_aH_bSiMe_3$), 2.69 (m, $C_5CH_2CH_3$), 2.23, 2.22, 2.14, 2.13, 1.74, 1.65, 1.60, 1.55 (s, 3 each, C_5CH_3), 1.93 (d, 1, J_{HH} = 12 Hz, $CH_aH_bSiMe_3$), 0.81 (m, $C_5CH_2CH_3$), 0.24 (s, 9, $SiMe_3$); $^{13}C\{^1H\}$ NMR (toluene-d_8) δ 167.4 (CHO), 120–124 (ring carbons), 55.3 (CH_2SiMe_3), 22.1–18.7 ($C_5CH_2CH_3$ carbons), 14.7, 14.1, 12.1–11.1 (C_5CH_3 carbons), 3.15 ($SiMe_3$).

Preparation of $Ta_2Cp'_2Cl_4(H)(O)(CHPMe_3)$. PMe_3 (0.2 mL, 2.6 mmol) was added to a solution of $Ta_2Cp'_2Cl_4H(CHO)$ (0.83 g, 1 mmol) in 50 mL of benzene. The color changed from orange to yellow in 0.5 h. Solvent was removed in vacuo, leaving crude, yellow $Ta_2Cp'_2Cl_4(H)(O)(CHPMe_3)$. Recrystallization from toluene/pentane gave 0.76 g (84%) yellow crystals in two crops: ^1H NMR ($CDCl_3$) δ 9.84 (dd, 1, J_{HH} = 5 Hz, J_{HP} = 2 Hz, TaH), 2.47 (m, 1, $C_5CH_2CH_3$), 2.44 (m, 1, $C_5CH_2CH_3$), 2.21 (q, 2, $C_5CH_2CH_3$), 2.19–2.13 (6 singlets, 24 total, C_5CH_3), 1.69 (d, 9, J_{HP} = 12 Hz, PMe_3), 1.44 (dd, 1, J_{PH} = 13 Hz, J_{HH} = 5 Hz, $CHPMe_3$), 1.05 (t, 3, $C_5CH_2CH_3$), 0.99 (t, 3, $C_5CH_2CH_3$); $^{31}P\{^1H\}$ NMR ($CHCl_3$) δ 22.5. Anal. Calcd for $Ta_2C_{26}H_{45}Cl_4OP$: C, 34.38; H, 4.99. Found: C, 34.47; H, 5.10. $Ta_2Cp'_2Cl_4(H)(O)(^{13}CHPMe_3)$ was prepared similarly from $Ta_2Cp'_2Cl_4(H)(^{13}CHO)$ and PMe_3 in benzene: ^{13}C NMR ($CDCl_3$, gated proton decoupled) δ 94.3 (ddd, J_{CP} = 44 Hz, J_{CH} = 122 Hz, J_{CH} = 10 Hz, $CHPMe_3$).

Preparation of $[Ta(\eta^5\text{-}C_5Me_4R)Cl_2H]_2(py)$. Pyridine (1.48 mmol) was added to an incompletely dissolved sample of $[TaCp''Cl_2H]_2$ (0.59 g) in 50 mL of toluene. The starting material dissolved to give a deep green solution, which was filtered and concentrated to ~35 mL. Pentane (~15 mL) was added and the reaction was cooled to −30 °C. The product crystallized as dark green, almost black crystals (0.6 g, 92%). It is less soluble than the starting material (in the absence of excess pyridine) in benzene or toluene. Variable amounts of pyridine of crystallization can be observed in the NMR spectra: ^1H NMR (C_6D_6) δ 9.61, 8.87, 6.78, 6.76, 6.59 (m, 1 each, py), 2.3, 2.16 (s, inequivalent Cp″ groups), 0.102 (s, 1, TaH). The other hydride resonance could not be found. In bromobenzene both hydride resonances could be found at 0.28 and 0.46 ppm. IR (Nujol) 1625 cm^{-1} (TaH). Anal. Calcd for $Ta_2C_{27}H_{41}NCl_4$: C, 36.71; H, 4.69; N, 1.59. Found: C, 37.22; H, 4.69; N, 2.00. Calcd for $Ta_2C_{28}H_{42}N_{1.2}Cl_3(1.2py)$: C, 37.8; H, 4.70; N, 1.87.

$[Ta(Cp')Cl_2H]_2(py)$ and deuterated derivatives were prepared similarly. ^1H NMR (C_6D_6) δ 9.719, 8.938, 6.733, 6.600, 6.382 (br, 1 each, pyridine), 2.63 (m, Cp CH_2CH_3), 2.443, 2.403, 2.367, 2.341, 2.301, 2.225, 2.110 (s, Cp CH_3), 0.863 (m, Cp CH_2CH_3), 0.287 (br s, 1, MH); IR (Nujol) 1625 (s, br, MH), 1165 cm^{-1} (s, br, MD).

Preparation of $TaCp^sCl_3(CH_2SiMe_3)$. $TaCl_4(CH_2SiMe_3)$ (4.1 g, 10.0 mmol) was dissolved in 60 mL of diethyl ether and the solution was cooled to −30 °C. Solid $LiCp^s$ (2.16 g, 10.0 mmol) was added all at once. After the solution was stirred at room temperature for 1.5 hours it was filtered. The filtrate was concentrated in vacuo and pentane was added. Cooling to −30 °C gave orange crystals (4.46 g, 76%) in two crops: ^1H NMR (C_6D_6) δ 6.56 (d, 2, C_5H_3), 6.42 (t, 1, C_5H_3), 1.83 (s, 2, CH_2SiMe_3), 0.46 (s, 9, CH_2SiMe_3), 0.20 (s, 18, $C_5(SiMe_3)_2$).

Preparation of $[TaCp^sCl_2H]_2$. $TaCp^sCl_3(CH_2SiMe_3)$ (1.25 g, 2.14 mmol) was dissolved in 50 mL of pentane and the solution was cooled to −30 °C. A solution of $ZnPr_2$ (0.20 g, 1.83 mmol) in 20 mL of pentane was added over 1 h. The purple solution was filtered and its volume reduced to ~10 mL in vacuo. It was then treated with H_2 (3 atm) in a glass bomb for 24 h. The green solution was stripped to dryness and the product recrystallized from pentane at −30 °C to give 0.65 (70%) green crystals: ^1H NMR (C_6D_6) δ 10.27 (s, 1, TaH), 7.06 (br s, 2, C_5H_3), 6.52 (br s, 1, C_5H_3), 0.29 (s, 18, $SiMe_3$).

Preparation of $Ta_2Cp^s_2Cl_4(H)(^{13}CHO)$ and $Ta_2Cp^s_2Cl_4(H)(O)(^{13}CHPMe_3)$. $[TaCp^sCl_2H]_2$ (0.090 g, 0.1 mmol) was dissolved in 20 mL of diethyl ether. The solution was degassed twice and ^{13}CO (5.6 mL, 0.5 mmol) added by Toepler pump at −78 °C. The solution was allowed to warm up to 0 °C and was stirred at this temperature for 2 h. The solvent was removed in vacuo and the residue was dissolved in C_6D_6: ^{13}C NMR (gated) δ 189.3 (d, J_{CH} = 185 Hz, CHO), 161.8 (d, J_{CH} = 177 Hz, CHO). Addition of excess PMe_3 (25 μL, 0.25 mmol) to the NMR sample caused a color change from dark orange to yellow: $^{13}C\{^1H\}$ NMR δ 93.8 (d, J_{CP} = 42.3 Hz, $CHPMe_3$).

Preparation of Mixtures of Cp^s_2, Cp'_2, and $Cp'Cp^s$ Complexes. A mixture of $TaCp^sCl_2$(propylene) (0.68 g, 1.37 mmol) and $TaCp'Cl_2$(propylene) (0.61 g, 1.37 mmol) dissolved in 15 mL of pentane was treated with H_2 (3 atm) for 24 h. The resulting green solution was stripped to dryness to give a green solid: ^1H NMR (C_6D_6) δ 10.59 (s, relative intensity 4, $Ta_2Cp'Cp^sCl_4H_2$), 10.42 (s, relative intensity 2, $Ta_2Cp'_2Cl_4H_2$), 10.28 (s, relative intensity 1, $Ta_2Cp^s_2Cl_4H_2$).

A sample (0.25 g) of the above mixture was treated with 1.2 equiv of ^{13}CO as in the previous experiment. The resulting orange solution was stripped to an oil, which was dissolved in C_6D_6: ^{13}C NMR (gated decoupled) δ 189.2 (d, J_{CH} = 183 Hz, Cp^s_2CHO), 168.1 (d, J_{CH} = 177 Hz, Cp'_2CHO and $Cp'Cp^sCHO$ (overlapping)), 161.7 (d, J_{CH} = 181 Hz, Cp^s_2CHO), 160.1 (d, J_{CH} = 179 Hz, $Cp'Cp^sCHO$), 151.9 (d, J_{CH} = 181 Hz, $Cp'Cp^sCHO$); see Figure 7b.

The NMR sample was then treated with excess PMe_3 (25 μL, 0.25 mmol). The color of the solution changed from dark orange to yellow: $^{13}C\{^1H\}$ NMR δ 96.2 (d, J_{CP} = 42 Hz, $Cp'Cp^sCHPMe_3$), 94.3 (d, J_{CP} = 42 Hz, Cp'_2CHPMe_3), 93.9 (d, J_{CP} = 42 Hz, $Cp^s_2CHPMe_3$); see Figure 7c.

Reaction of a Mixture of $Ta_2Cp'_2Cl_4H_2$ and $Ta_2Cp^s_2Cl_4H_2$ with ^{13}CO. A mixture of $Ta_2Cp'_2Cl_4H_2$ (0.08 g, 0.1 mmol) and $Ta_2Cp^s_2Cl_4H_2$ (0.09 g, 0.1 mmol) was dissolved in 30 mL of diethyl ether and the solution was degassed twice. ^{13}CO (6.7 mL, 0.30 mmol) was transferred into the reaction flask by Toepler pump and the solution was stirred at 0 °C for 4 h. The solvent was then stripped off and the residue dissolved in C_6D_6: $^{13}C\{^1H\}$ NMR δ 189.2 (Cp^s_2CHO), 168.5 (Cp'_2CHO), 161.7 (Cp^s_2CHO). Excess PMe_3 (25 μL, 0.25 mmol) was added to the NMR tube: $^{13}C\{^1H\}$ NMR δ 94.3 (d, J_{CP} = 44 Hz, Cp'_2CHPMe_3), 93.9 (d, J_{CP} = 42.3 Hz, $Cp^s_2CHPMe_3$).

In a second experiment, using a mixture of 0.04 g of $Ta_2Cp'_2Cl_4H_2$ and 0.05 g of $Ta_2Cp^s_2Cl_4H_2$ and a 10-fold excess of ^{13}CO (22.4 mL, 1 mmol), an identical result with the above was obtained.

In a third experiment a mixture of $Ta_2Cp'_2Cl_4H_2$ (0.08 g, 0.1 mmol) and $Ta_2Cp^s_2Cl_4H_2$ (0.09 g, 0.1 mmol) in diethyl ether was treated with ^{13}CO (5.6 mL, 0.25 mmol) at −78 °C for 24 h until the solution was purple. Excess ^{13}CO was then pumped away and the solution allowed to warm to room temperature. A ^{13}C NMR spectrum of the products (in C_6D_6) was essentially the same as in the two previous experiments.

Observation of $[TaCp'Cl_2H]_2(CO)$ by Low-Temperature Infrared Spectroscopy. A solution of $[TaCp'Cl_2H]_2$ (20 mg, 0.025 mmol) in ~5 mL of dimethyl ether was stirred at −78 °C for 2 h under 1 atm of CO. This yielded a deep purple solution, which was transferred, via an all metal and glass system (incorporating a stainless steel bellows valve) cooled to −78 °C, into the precooled reservoir of the infrared cell. The dimethyl ether was then pumped off at −78 °C, leaving a purple film on

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[21] Shriver, D. F. "The Manipulation of Air-Sensitive Compounds"; McGraw-Hill: New York, 1969; p 95.

the NaCl window: IR 1939 (ν_{CO}), 1875 ($\nu_{^{13}CO}$), 1599 (ν_{TaH}), 1560 cm^{-1} (ν_{TaH}); see Figure 9.

Observations of $[TaCp'Cl_2H]_2(^{13}CO)$ by ^{13}C NMR. A solution of $[TaCp'Cl_2H]_2$ (40 mg, 0.050 mmol) in toluene-d_8 was transferred into an NMR tube equipped with a greaseless stopcock and containing a tiny magnetic stir bar. The solution was degassed three times and then cooled to −78 °C. Excess ^{13}CO (11.2 mL, 0.5 mmol) was then added by using a Toepler pump, and the solution was stirred at −78 °C for 2 days. The stir bar was lifted out with a magnet and the tube was evacuated and sealed: ^{13}C NMR (gated decoupled, −70 °C) δ 238.2 (s, $[TaCp'Cl_2H]_2(^{13}CO)$, 167.2 (d, J_{CH} = 171 Hz, $Ta_2Cp'_2Cl_4(H)(^{13}CHO)$.

Reaction of $Ta_2Cp'_2Cl_4(H)(CHO)$ with $AlCl_3$. $AlCl_3$ (0.2 g, 1.5 mmol) was added to a toluene solution of $Ta_2Cp'_2Cl_4(H)(CHO)$ (0.83 g, 1 mmol) along with 20 μL (0.11 mmol) of nonane as an internal standard. Some $AlCl_3$ did not dissolve. The mixture was stored at 0 °C for 16 h, and then a sample was removed for GLC analysis. Methane (0.3 mmol) was found in solution.

Reaction of $Ta_2Cp'_2Cl_4(H)(CHO)$ with $AlCl_3$ in the Presence of H_2. $Ta_2Cp'_2Cl_4(H)(CHO)$ (0.4 g, 0.48 mmol) and $AlCl_3$ (9.08 g, 0.6 mmol) were added to a round-bottom vacuum flask. The flask was evacuated and cooled to −78 °C. Chlorobenzene (20 mL) saturated with H_2 was added to the first flask along with approximately 2 mmol of H_2 gas. The flask was warmed to 90 °C and magnetically stirred for 3 h. The reaction mixture was freeze–thaw degassed four times and the gases along with 6 mL (0.27 mmol) of isobutylene were transferred to a second flask by using a Toepler pump. By GLC the yield of methane was 70%. No C_2H_4 or C_2H_6 was found. A slightly lower yield of methane was obtained (60% based on integration vs internal C_2H_4) when the amount of dihydrogen was reduced by half. The experiment was performed as above.

Reaction of $Ta_2Cp'_2Cl_4(H)(^{13}CHO)$ with $AlCl_3$ in D_2. An all-glass reaction vessel was constructed that consisted of a 25-mL round-bottom flask, a 5-mL solvent side arm, a 100-mL gas bulb with stopcock, and a thick-walled NMR tube on a side arm. $Ta_2Cp'_2Cl_4(H)(^{13}CHO)$ (0.08 g, 0.1 mmol) and excess $AlCl_3$ were added to the reaction vessel. To the solvent container was added 0.5 mL of toluene-d_8. The gas bulb was filled with D_2 at 1 atm pressure. The solvent in the side arm was frozen and the reaction vessel was evacuated. The D_2 was admitted to the vessel and solvent was distilled over into the flask. The mixture was stirred and heated to 80 °C. The color of the solution changed from orange to yellow to green. The NMR tube was cooled in liquid nitrogen and the tube was flame sealed. A ^{13}C NMR spectrum at 62.8 MHz showed a singlet due to $^{13}CH_4$ at 2.80 ppm and a 1:1:1 triplet ascribed to $^{13}CH_3D$ at 2.60 ppm. If we assume that the peak areas are indicative of the relative amounts, then it is a 35:65 mixture of $^{13}CH_4$ and $^{13}CH_3D$, respectively. No evidence for a quintet slightly further upfield assignable to $^{13}CH_2D_2$ could be found, but poor signal-to-noise ratios prevented our being certain none was produced.

Reaction of $Ta_2Cp'_2Cl_4(H)(CHO)$ with Aqueous HCl. $Ta_2Cp'_2Cl_4(H)(CHO)$ (0.09 g, 0.108 mmol) was added to a vial along with 0.2 mL of pentanediol. The solution was cooled to 0 °C. Aqueous HCl (12 N, 60 μL, 0.72 mmol) and ethanol (6.2 μL, 0.106 mmol) were added. The solution was slowly warmed to 25 °C. Methanol was measured by GLC on Carbowax 20M with ethanol as the internal standard (0.088 mmol, 82%).

In a separate experiment $Ta_2Cp'_2Cl_4(H)(CHO)$ (0.83 g, 0.1 mmol) in 1-propanol was treated with 0.5 mL of 12 N HCl (aqueous) (6 mmol). After 0.5 h a 1 μL sample was withdrawn for GLC analysis. Methanol (4.1 μL, 0.1 mmol) was added to the reaction mixture and another 1-μL sample was withdrawn for GLC analysis. Comparison of peak areas indicated a 79% yield of methanol.

Reaction of $Ta_2Cp'_2Cl_4(H)(CHO)$ with Anhydrous HCl. A solution of $Ta_2Cp'_2Cl_4(H)(CHO)$ (0.42 g, 0.5 mmol) in 100 mL of toluene was cooled to −78 °C. HCl (25 mL, 1.1 mmol) was added to the flask by syringe. The reaction was slowly warmed to 22 °C with stirring. The color changed from orange-red to red and, after several hours at room temperature, to orange. The volume was reduced to approximately 80 mL under vacuum. The solution was transferred to another flask by cannula. Pentane (100 mL) was added. The solution was cooled to 0 °C for 12 h. The reaction mixture was filtered and the solvent was removed from the filtrate in vacuo. An orange solid formed as the solution was concentrated (0.3 g): ^{1}H NMR (C_6D_6) δ 4.38 (s, OCH_3), 2.68 (m, $C_5CH_2CH_3$), 2.338, 2.234, 2.213, 2.136, 2.098 (s, C_5CH_3), 0.763 (t, $C_5CH_2CH_3$); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 133.7, 131.3, 130.1, 128.6, 128.3 (ring carbons), 21.2, 20.4 ($C_5CH_2CH_3$ carbons), 15.2 ($C_5CH_2CH_3$ carbons), 13.0, 12.7, 12.5, 12.0 (C_5CH_3 carbons). The ^{13}C NMR spectrum of a sample of $Ta_2Cp'_2Cl_4H(^{13}CHO)$ in bromobenzene to which 2 equiv of HCl had been added showed (besides a peak due to some unreacted starting material) a methoxide carbon peak at 66.84 ppm (J_{CH} = 146 Hz, major product) and another at 62.85 ppm (J_{CH} = 146 Hz, minor product).

If only 1 equiv of HCl is used, half the starting material remains.

Reaction of $Ta_2Cp'_2Cl_4(H)(CHO)$ with $AlMe_3$. $AlMe_3$ (0.14 g, 2 mmol) was added to a toluene solution of $Ta_2Cp'_2Cl_4(H)(CHO)$ (0.42 g, 0.5 mmol) at −30 °C. The color changed from red to clear yellow. Solvent was removed in vacuo and the yellow oil was dissolved in C_6D_6. An ^{1}H NMR spectrum showed a hydride resonance at 8.3 ppm and a formyl proton resonance at 6.6 ppm (d, J = 4 Hz).

In a separate experiment excess $AlMe_3$ was added to a solution of $Ta_2Cp'_2Cl_4(H)(^{13}CHO)$ in C_6D_6. The ^{13}C NMR spectrum showed formyl carbon resonances at 227.4 ppm (d, J = 156 Hz) and 214.36 ppm (dd, J = 152.6, 9.1 Hz).

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Registry No. 1, 84929-11-3; **1** (^{13}C labeled), 84929-12-4; **4**, 74167-06-9; **4** (dideuterated), 84944-10-5; $Ta_2Cp'_2Cl_3(H)(CHO)(CH_2SiMe_3)$, 84944-11-6; $Ta_2Cp'_2Cl_4(H)(O)(CHPMe_3)$, 74167-07-0; $[TaCp'Cl_2H]_2(py)$, 84944-12-7; $TaCp^sCl_3(CH_2SiMe_3)$, 84929-00-0; $[TaCp^sCl_2H]_2$, 84929-01-1; $Ta_2Cp^s_2Cl_4(H)(^{13}CHO)$, 84944-13-8; $Ta_2Cp^s_2Cl_4(H)(O)(^{13}CHPMe_3)$, 84929-02-2; $Ta_2Cp'Cp^sCl_4H_2$, 84929-03-3; $[TaCp'Cl_2H]_2$, 74153-80-3; $Ta_2Cp'_2Cl_4(H)(^{13}CHO)$, 84944-14-9; $[TaCp'Cl_2D]_2$, 84929-04-4; $Ta_2Cp'_2Cl_4(H)(O)(^{13}CHPMe_3)$, 84929-06-6; $TaCl_4(CH_2SiMe_3)$, 54773-24-9; $TaCp^sCl_2B$ (B = propylene), 84929-07-7; $TaCp'Cl_2B$ (B = propylene), 84929-08-8; $Ta_2Cp^s_2Cl_4(H)(CHO)$, 84929-09-9; $Ta_2Cp'Cp^sCl_4(H)(O)(CHPMe_3)$, 84929-10-2; $Ma(CH_2SiMe_3)_2B$ (B = dioxane), 84929-05-5; CO, 630-08-0; $LiCp^s$, 56742-80-4; ZnPra, 628-91-1; $AlCl_3$, 7446-70-0; CH_4, 74-82-8; $^{13}CH_4$, 6532-48-5; $^{13}CH_3D$, 2758-34-1; HCl, 7647-01-0; $AlMe_3$, 75-24-1.