Organometallics 1988, *7*, 436–441

Acknowledgment. We thank the National Science Foundation (Grant No. CHE8519557) for financial support, Dow Corning Corp. for a fellowship to P.E.R., and Johnson Matthey for a loan of iridium and rhodium salts.

Registry No. **3a**, 111765-82-3; **4**, 111495-67-1; **4**$\cdot 6CH_2Cl_2$, 111612-94-3; **5**, 111495-69-3; **6**, 111495-71-7; **7**, 111495-73-9; methyltriphenylarsonium iodide, 1499-33-8.

Supplementary Material Available: Listings of all bond distances, all bond angles, hydrogen atom positions, and anisotropic thermal parameters and ^{31}P NMR spectra for **4** (7 pages); a listing of structure factor amplitudes for **4** (37 pages). Ordering information is given on any current masthead page.

Tungsten and Molybdenum Alkylidyne Complexes Containing Bulky Thiolate Ligands

John S. Murdzek, Lauren Blum, and Richard R. Schrock*

Department of Chemistry, 6-331, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received June 29, 1987

Complexes of the type $Mo(C\text{-}t\text{-}Bu)(TMT)_3$ and $Mo(C\text{-}t\text{-}Bu)(TIPT)_3$ (TMT = 2,4,6-trimethylbenzenethiolate; TIPT = 2,4,6-triisopropylbenzenethiolate) can be prepared by adding 3 equiv of LiSAr (SAr = TMT or TIPT) to $Mo(C\text{-}t\text{-}Bu)Cl_3(dme)$. The TMT derivative is believed to be dimeric on the basis of NMR spectra. Reactions between $M(C\text{-}t\text{-}Bu)Cl_3(dme)$ (M = Mo or W), ArSH, and NEt_3 yield complexes of the type $[Et_3NH][M(C\text{-}t\text{-}Bu)(SAr)_3Cl]$. $W(C\text{-}t\text{-}Bu)(SAr)_3$ complexes can be prepared by removing chloride ion from the $[Et_3NH][W(C\text{-}t\text{-}Bu)(SAr)_3Cl]$ species with zinc chloride. $M(C\text{-}t\text{-}Bu)(SAr)_3$ complexes do not react with 3-hexyne, 2-butyne, or phenylacetylene, and only minute traces of 3-heptyne metathesis products are observed after 3 days at 25 °C. The reaction between $W(C_3Me_3)Cl_3$ and LiTIPT yields $W(C_3Me_3)(TIPT)_3$ (in situ), the reaction between $W(C_3Me_3)Cl_3$, TIPTH, and NEt_3 (or that between $W(C_3Me_3)(TIPT)_3$ and Et_3NHCl) gives $[Et_3NH][W(CMe)(TIPT)_3Cl]$, and the reaction between the η^3-cyclopropenyl complex $W(C_3\text{-}t\text{-}BuMe_2)Cl_3(py)_2$ and LiTMT yields a mixture of $W(CMe)(TMT)_3(py)$ and $W(C\text{-}t\text{-}Bu)(TMT)_3(py)$. Both $Mo(CPr)(TIPT)_3$ and $W(CMe)(TIPT)_3$ are stable and isolable. We conclude from these studies that $M(CR)(SAr)_3$ complexes react too slowly with ordinary acetylenes to be active catalysts, either because coordination of sulfur (in a dimer) competes effectively with coordination of the acetylene or because the metal is simply not electrophilic enough, or both.

Introduction

We have discovered that some complexes of the type $M(CR)(OR')_3$ (M = Mo, W; R = alkyl; OR′ = (e.g.) O-*t*-Bu, $OCMe_2(CF_3)$, O-2,6-C_6H_3-*i*-Pr_2) will metathesize internal acetylenes.[1] This activity depends sensitively upon M and OR′. For example, $Mo(C\text{-}t\text{-}Bu)(O\text{-}t\text{-}Bu)_3$ does not react with internal acetylenes,[1b] while $W(C\text{-}t\text{-}Bu)(O\text{-}t\text{-}Bu)_3$ reacts extremely rapidly to give a new alkylidyne complex derived from half the acetylene.[1a,e] If more electron-withdrawing alkoxide ligands are employed, then molybdenum species such as $Mo(C\text{-}t\text{-}Bu)[OCMe(CF_3)_2]_3$ become active catalysts.[1b] Metallacyclobutadiene intermediates sometimes can be observed, and some tungsten complexes are quite stable;[1c] in the case of $W(C_3R_3)(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2]_3$, the rate-limiting step of the acetylene metathesis reaction consists of loss of an acetylene from the metallacyclic ring.

Table I. Selected ^{13}C NMR Data for Thiolate Complexes[a]

compound	$\delta(C_\alpha)$
$[Mo(C\text{-}t\text{-}Bu)(TMT)_3]_2$	336.0
$[Et_3NH][Mo(C\text{-}t\text{-}Bu)(TMT)_3Cl]$	316.3
$Mo(C\text{-}t\text{-}Bu)(TIPT)_3$	341.5
$Mo(CPr)(TIPT)_3$	333.6
$[W(C\text{-}t\text{-}Bu)(TMT)_3]_2$	324.3
$W(C\text{-}t\text{-}Bu)(TIPT)_3$	329.4
$W(CMe)(TIPT)_3$	312.1
$W(CMe)(TMT)_3(py)$	308.2
$[Et_3NH][W(C\text{-}t\text{-}Bu)(TMT)_3Cl]$	304.0[b]
$[Et_3NH][W(C\text{-}t\text{-}Bu)(TIPT)_3Cl]$	306.9
$[Et_3NH][W(CMe)(TIPT)_3Cl]$	294.8

[a] Solvent = CD_2Cl_2 at T = 298 K unless otherwise noted. [b] J_{CW} = 216 Hz.

An important question is how the behavior of other complexes of the type $M(CR)X_3$ (X = (e.g.) halide, amide, thiolate) compare with that observed for the alkoxide complexes. So far we know that tungsten halide derivatives will form tungstacyclobutadiene complexes[2] but will not in general metathesize ordinary acetylenes; cyclopentadienyl complexes are formed instead.[2,3] We also know that $W(CEt)(NMe_2)_3$ will not metathesize ordinary acetylenes,[4] although it is not known whether steric or electronic factors are the primary cause of the lower activity. $M(C\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)_3$[1b,5] complexes also will not

---

(1) (a) Schrock, R. R. *J. Organomet. Chem.* **1986**, *300*, 249. (b) McCullough, L. G.; Schrock, R. R.; Dewan, J. C.; Murdzek, J. S. *J. Am. Chem. Soc.* **1985**, *107*, 5987. (c) Churchill, M. R.; Ziller, J. W.; Freudenberger, J. H.; Schrock, R. R. *Organometallics* **1984**, *3*, 1554. (d) Freudenberger, J. H.; Schrock, R. R.; Churchill, M. R.; Rheingold, A. L.; Ziller, J. W. *Organometallics* **1984**, *3*, 1563. (e) Schrock, R. R. *Acc. Chem. Res.* **1986**, *19*, 342.

(2) Schrock, R. R.; Pedersen, S. F.; Churchill, M. R.; Ziller, J. W. *Organometallics* **1984**, *3*, 1574.

(3) Latham, I. A.; Sita, L. R.; Schrock, R. R. *Organometallics* **1986**, *5*, 1508.

(4) (a) It has been shown that $W(C\text{-}t\text{-}Bu)(NMe_2)_3$[5] and related complexes (e.g., $W(C\text{-}t\text{-}Bu)(N\text{-}i\text{-}Pr_2)_3$[4b]) will metathesize 3-heptyne erratically, if such species are prepared from $W(C\text{-}t\text{-}Bu)(dme)Cl_3$. Impurities such as "$W(C\text{-}t\text{-}Bu)(NR_2)_2Cl$" must be responsible since $W(CEt)(NMe_2)_3$ prepared from $W(CEt)(O\text{-}t\text{-}Bu)_3$ is inactive.[4c] (b) Leigh, G. J.; Rahman, M. T.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun.* **1982**, 541. (c) M. L. Listemann, Ph.D. Thesis, M.I.T., 1985.

(5) Schrock, R. R.; Clark, D. N.; Sancho, J.; Wengrovius, J. H.; Rocklage, S. M.; Pedersen, S. F. *Organometallics* **1982**, *1*, 1645.

0276-7333/88/2307-0436$01.50/0

metathesize ordinary acetylenes under mild conditions. Since oxygen ligands can be viewed as being overall more electronegative than alkyl or amido ligands, we thought it would be interesting to known whether thiolate ligands, which should be considerably less electronegative than alkoxide ligands in a broad sense, also would deactivate the metal toward metathesis reactions. The results of such a study involving 2,4,6-triisopropylbenzenethiolate (TIPT) and 2,4,6-trimethylbenzenethiolate (TMT) ligands are reported here.

Results and Discussion

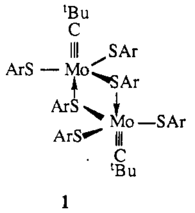
Molybdenum Complexes. Molybdenum complexes of the type Mo(C-*t*-Bu)(SAr)$_3$ can be prepared straightforwardly as shown in eq 1. The yields are high according

$$\mathrm{Mo(C\text{-}}t\mathrm{\text{-}Bu)Cl_3(dme)} + 3\mathrm{LiSAr} \xrightarrow[-3\mathrm{LiCl{-}dme}]{\text{ether, } -30\ ^\circ\mathrm{C}} \mathrm{Mo(C\text{-}}t\mathrm{\text{-}Bu)(SAr)_3} \tag{1}$$

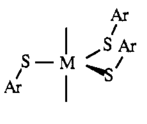
to ^{1}H NMR spectra of the crude reaction product. Pure products can be isolated in 50–70% yield, the higher yield being for the significantly less soluble TMT complex. Mo(C-*t*-Bu)(TMT)$_3$ is not very soluble in pentane, or even in dichlormethane (~50 mg in 3 mL). The Mo(C-*t*-Bu)(TIPT)$_3$ complex is significantly more soluble in both. We felt that this solubility difference was beyond the difference to be expected between analogous monomeric complexes and that the TMT complex (at least) therefore was likely to be a dimer.

Proton NMR spectra of the TIPT complex are straightforward. Only one type of TIPT ligand is present on the ^{1}H NMR time scale in CD$_2$Cl$_2$, even at −60 °C. The ^{13}C NMR spectrum shows an alkylidyne C$_\alpha$ signal at 341.5 ppm (Table I). This chemical shift should be compared with that for C$_\alpha$ in Mo(C-*t*-Bu)(DIPP)$_3$ (DIPP = 2,6-diisopropylphenoxide) at 320 ppm.[1b]

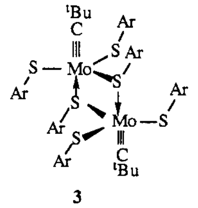
Proton NMR spectra of Mo(C-*t*-Bu)(TMT)$_3$ are considerably more complex than those of Mo(C-*t*-Bu)(TIPT)$_3$. At 100 °C the ^{1}H NMR spectrum of Mo(C-*t*-Bu)(TMT)$_3$ shows only one type of TMT ligand to be present on the NMR time scale. However, at 25 °C the spectrum contains broad methyl and aromatic proton peaks, and at −60 °C seven unique methyl peaks and five aromatic proton resonances are observed. This result cannot be attributed to the presence of geometric isomers, as only one *tert*-butyl resonance in the ^{1}H NMR spectrum is observed at −60 °C. Therefore, we propose that the structure of Mo(C-*t*-Bu)(TMT)$_3$ (**1**) is overall analogous to the structure of W(CMe)(O-*t*-Bu)$_3$,[6] a dimer formed by bridging the metals with TMT ligands. At 100 °C the dimer must be breaking up into monomers at a rate that is rapid on the NMR time scale. Either Mo(C-*t*-Bu)(TIPT)$_3$ is a monomer, or it is also a dimer, but one that breaks up much more rapidly than the [Mo(C-*t*-Bu)(TMT)$_3$]$_2$ complex for steric reasons, even at −60 °C.



1



2



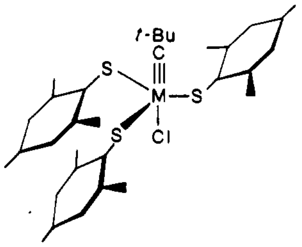
3

In all known TBP structures containing at least three relatively bulky arenethiolate ligands,[7] the three equatorial arenethiolate ligands are arranged so that two point toward one axial position and the third points away ("two up, one down") as shown schematically in **2**. The plane of the aryl ring is roughly perpendicular to the plane that contains the bonds between the metal and an axial ligand and the bond between the metal and the sulfur to which the ring is attached. M–S–C angles are typically in the range 110–120°. We believe the same is likely to be true here, i.e., that the structure of [Mo(C-*t*-Bu)(TMT)$_3$]$_2$ is **3** in which there are three independent thiolate ligands in the absence of rotation about the M–S bond. In this particular circumstance steric crowding could be so severe that the aryl rings also cannot rotate about the S–C bond, thereby giving rise to a structure that contains only a C_2 axis. If all Mo–S and S–C rotations are slow on the NMR time scale, then nine methyl peaks and six aromatic proton resonances would be observed. If rotation about the S–C bond is facile, then six methyl peaks would be observed. Observation of seven methyl peaks and five aromatic proton resonances suggests that S–C bond rotation is slow and that there is some overlap of the methyl resonances.

If Mo(C-*t*-Bu)Cl$_3$(dme) is added to a mixture of TMTH and NEt$_3$ (3 equiv of each) in ether, then a salt is formed (eq 2) that is soluble in aromatic solvents. Although at

$$\mathrm{Mo(C\text{-}}t\mathrm{\text{-}Bu)Cl_3(dme)} + 3\mathrm{TMTH} + 3\mathrm{NEt_3} \xrightarrow[-2\mathrm{Et_3NHCl{-}dme}]{\text{ether, } -30\ ^\circ\mathrm{C}} [\mathrm{Et_3NH}][\mathrm{Mo(C\text{-}}t\mathrm{\text{-}Bu)(TMT)_3Cl}] \tag{2}$$

room temperature its ^{1}H NMR spectrum shows only two TMT methyl signals in the ratio of 18:9, the low-temperature spectrum (253 K) shows five TMT methyl signals in the ratio of 2:2:2:2:1. If we assume that the three TMT ligands in [Mo(C-*t*-Bu)(TMT)$_3$Cl]$^-$ are bound in equatorial positions ("two up, one down" or vice versa), then the observed ratio of methyl signals at low temperature can be explained only if rotation about the Mo–S and S–C bonds is slow on the NMR time scale in structure **4**. (The ortho methyl groups on the two equivalent TMT ligands divide into an "inside" set and an "outside" set.) At higher temperatures rotation about the M–S and S–C bonds must be relatively fast. Loss of chloride ion also might be responsible for equilibration of the methyl groups since addition of zinc chloride to [Mo(C-*t*-Bu)(TMT)$_3$Cl]$^-$ yields [Mo(C-*t*-Bu)(TMT)$_3$]$_2$ (eq 3). Zinc chloride might simply be serving as a scavenger of free chloride ion.



4

$$[\mathrm{Et_3NH}][\mathrm{Mo(C\text{-}}t\mathrm{\text{-}Bu)(TMT)_3Cl}] \xrightarrow[-[\mathrm{Et_3NH}][\mathrm{ZnCl_3}]]{+\mathrm{ZnCl_2\ in\ CH_2Cl_2}} 0.5[\mathrm{Mo(C\text{-}}t\mathrm{\text{-}Bu)(TMT)_3}]_2 \tag{3}$$

Tungsten Complexes. Addition of LiTMT or LiTIPT to W(C-*t*-Bu)Cl$_3$(dme) does not lead to complexes of the

---

[6] Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *Inorg. Chem.* **1983**, *22*, 2903.

[7] (a) Koch, S. A.; Millar, M. *J. Am. Chem. Soc.* **1983**, *105*, 3362. (b) Blower, P. J.; Dilworth, J. R.; Hutchinson, J. P.; Zubieta, J. A. *J. Chem. Soc., Dalton Trans.* **1985**, 1533. (c) Bishop, P. T.; Dilworth, J. R.; Hutchinson, J.; Zubieta, J. A. *J. Chem. Soc., Dalton Trans.* **1986**, 967. (d) Dilworth, J. R.; Hutchinson, J.; Zubieta, J. A. *J. Chem. Soc., Chem. Commun.* **1983**, 1034. (e) Walborsky, E. C.; Wigley, D. E.; Roland, E.; Dewan, J. C.; Schrock, R. R. *Inorg. Chem.* **1987**, *26*, 1615.

type W(C-*t*-Bu)(SAr)$_3$. However, if 3 equiv of thiol are employed in the presence of Et$_3$N, then anionic complexes of the type [Et$_3$NH][W(C-*t*-Bu)(SAr)$_3$Cl] (SAr = TMT or TIPT) can be isolated readily. It is possible that the analogous lithium salts are formed in reactions employing LiTMT or LiTIPT but that they are not as tractable as the ammonium salts.

The ^{1}H NMR spectrum of [Et$_3$NH][W(C-*t*-Bu)(TMT)$_3$Cl] at low temperature is analogous to that of [Et$_3$NH][Mo(C-*t*-Bu)(TMT)$_3$Cl], suggesting that its structure is 4 in which rotation about M–S and S–C bonds is slow on the NMR time scale. However, at 293 K four methyl resonances are present (instead of five) in a ratio of 4:2:2:1. This result could arise if rotation about the S–C bonds (but still not about the M–S bonds) were rapid, although it is more likely simply due to accidental overlap of resonances. Frequent overlap of resonances is further suggested by the fact that in C$_6$D$_6$ at 25 °C *five* methyl resonances are observed in a 2:2:2:1:2 ratio and two aromatic (meta) proton resonances in a 2:1 ratio.

In the ^{1}H NMR spectrum of [Et$_3$NH][W(C-*t*-Bu)(TIPT)$_3$Cl] at 293 K we observe eight isopropyl methyl group signals and five isopropyl methine proton signals. If the structure is analogous to 4, then the observed spectrum would be obtained without overlapping signals if rotation about the S–C bonds in the two equivalent thiolate ligands were slow and rotation about the S–C bond in the unique TIPT ligand were facile. If rotation about the S–C bond in the unique TIPT also were not facile (the more likely possibility in our opinion), then some signals would have to overlap in order to produce the observed spectrum. In short, the low-temperature structures of [W(C-*t*-Bu)(TMT)$_3$Cl]$^-$ and [W(C-*t*-Bu)(TIPT)$_3$Cl]$^-$ are likely to be analogous with rotations about S–C bonds and M–S bonds being slow on the NMR time scale, even at room temperature in the more crowded TIPT complex.

It *is* possible to prepare neutral tungsten complexes of the formula W(C-*t*-Bu)(SAr)$_3$, by adding zinc chloride to the anionic species (eq 4). [W(C-*t*-Bu)(TMT)$_3$]$_2$ also can be prepared as shown in eq 5, but W(C-*t*-Bu)(TIPT)$_3$ cannot be prepared by this method, probably because (Me$_3$Si)TIPT is relatively unreactive for steric reasons. The characteristics of the W(C-*t*-Bu)(SAr)$_3$ derivatives are analogous to those described above for the Mo species, a fact that suggests that at least the TMT derivative is a dimer. The TIPT derivative may also be a weakly associated dimer in the solid state, but for now we presume it to be a monomer.

$$[\mathrm{Et_3NH}][\mathrm{W(C\text{-}}t\mathrm{\text{-}Bu)(SAr)_3Cl}] + \mathrm{ZnCl_2} \xrightarrow{\mathrm{CH_2Cl_2}} [\mathrm{Et_3NH}][\mathrm{ZnCl_3}] + \mathrm{W(C\text{-}}t\mathrm{\text{-}Bu)(SAr)_3} \quad (4)$$

$$\mathrm{W(C\text{-}}t\mathrm{\text{-}Bu)Cl_3(dme)} + 3(\mathrm{Me_3Si})\mathrm{TMT} \rightarrow 3\mathrm{Me_3SiCl} + 0.5[\mathrm{W(C\text{-}}t\mathrm{\text{-}Bu)(TMT)_3}]_2 \quad (5)$$

Evaluating Thiolate Complexes as Acetylene Metathesis Catalysts. The addition of 3-hexyne, 2-butyne, or phenylacetylene to the molybdenum and tungsten complexes M(C-*t*-Bu)(TIPT)$_3$ and [M(C-*t*-Bu)(TMT)$_3$]$_2$ resulted in the formation of some polymer, especially when the metal is tungsten and especially in dichloromethane. However, in no case were metathesis products observed, nor new alkylidyne complexes, nor metallacycles or other organometallic products. Over the long term (days), or at higher temperatures, the starting material gradually disappeared, but no products could be identified. Free thiol was commonly observed, we presume due to hydrolysis. We also could see only minute traces of the products of metathesis of 3-heptyne (20 equiv) in 3 days in dichloromethane in the presence of [Mo(C-*t*-Bu)(TMT)$_3$]$_2$, Mo(C-*t*-Bu)(TIPT)$_3$, or W(CMe)(TIPT)$_3$ (see below).

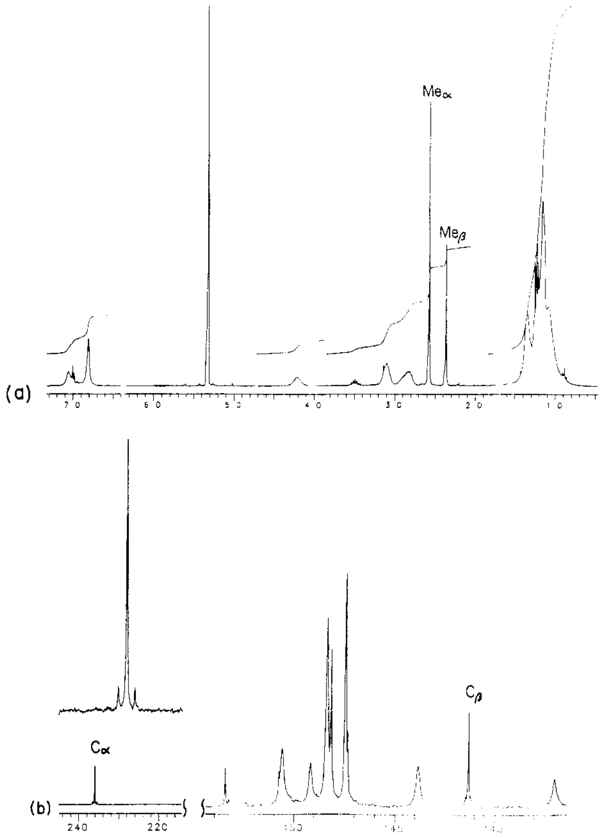


Figure 1. (a) ^{1}H NMR spectrum and (b) partial ^{13}C NMR spectrum of W(C$_3$Me$_3$)(TIPT)$_3$ in CD$_2$Cl$_2$.

One control experiment consisted of preparing the expected alkylidyne complex of one of the reactions between Mo(C-*t*-Bu)(SAr)$_3$ and an acetylene. It is known that Mo(C-*t*-Bu)[OCMe$_2$(CF$_3$)]$_3$ reacts with 4-octyne to give Mo(CPr)[OCMe$_2$(CF$_3$)]$_3$.[1b] Mo(CPr)(TIPT)$_3$ was prepared straightforwardly from Mo(CPr)[OCMe$_2$(CF$_3$)]$_3$ as shown in eq 6. Mo(CPr)(TIPT)$_3$ appears to be entirely analogous to Mo(C-*t*-Bu)(TIPT)$_3$. We see no evidence that it is especially unstable. Therefore, it could be observed if it were a product of the reaction between Mo(C-*t*-Bu)(TIPT)$_3$ and 4-octyne noted above.

$$\mathrm{Mo(CPr)[OCMe_2(CF_3)]_3} + 3\mathrm{LiTIPT} \xrightarrow[-3\mathrm{LiOCMe_2(CF_3)}]{\text{pentane}} \mathrm{Mo(CPr)(TIPT)_3} \quad (6)$$

The reaction between W(C$_3$Me$_3$)Cl$_3$ and LiTIPT led to a single product in a clean reaction. We have not been able to isolate this exceedingly soluble material (it may be an oil) but feel that it can be identified adequately by its ^{1}H and ^{13}C NMR spectra as the trimethyltungstacyclobutadiene complex shown in eq 7. Its ^{1}H NMR spectrum (Figure 1a) shows two resonances in a 2:1 ratio at 2.57 and 2.37 ppm that can be ascribed to α- and β-methyl groups in the trimethyltungstacycle (cf. $\delta(\mathrm{Me}_\alpha)$ and $\delta(\mathrm{Me}_\beta)$ of 3.22 and 2.16 ppm in W(C$_3$Me$_3$)[OCMe(CF$_3$)$_2$]$_3$ in C$_6$D$_6$,[1d] 3.58 and 2.90 ppm in W(C$_3$Me$_3$)(O-2,6-C$_6$H$_3$Me$_2$)$_3$ in CD$_2$Cl$_2$,[3,8] and 4.22 and 3.52 ppm in W(C$_3$Me$_3$)Cl$_3$ in CD$_2$Cl$_2$[3,8]). The ^{13}C NMR spectrum of W(C$_3$Me$_3$)(TIPT)$_3$ (Figure 1b)

$$\mathrm{W(C_3Me_3)Cl_3} + 3\mathrm{LiTIPT} \xrightarrow[-3\mathrm{LiCl}]{\text{ether, }-30\ ^\circ\mathrm{C}} \mathrm{W(C_3Me_3)(TIPT)_3} \quad (7)$$

---

(8) Me$_\alpha$ and Me$_\beta$ chemical shifts were not published in the preliminary communication.[3]

Table II. Comparison of ^{13}C NMR Chemical Shifts for Ring Carbons in $W(C_3Me_3)(TIPT)_3$ (Observed in Situ) with Those for Selected Other Tungstacyclobutadiene Complexes[a]

compound	$\delta(C_\alpha)$	$\delta(C_\beta)$	ref
$W(C_3Et_3)[OCH(CF_3)_2]_3$	242.9 (127)	147.3	1d
$W(C_3Me_3)[OCMe(CF_3)_2]_3$	239.9	133.5	1d
$W(C_3Et_3)(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_3$	244.9 (124)	136.6	1c
$W(C_3Me_3)(O\text{-}2,6\text{-}C_6H_3Me_2)_3$[b]	230.9 (129)	139.0	3
$W(C_3Me_3)Cl_3$[b]	257.9	152.1	3
$W(C_3Me_3)(S\text{-}2,4,6\text{-}C_6H_2\text{-}i\text{-}Pr_3)_3$[b]	236.1 (112)	141.3 (~25)	this work

[a] Solvent is C_6D_6 unless otherwise noted. Values for J_{CW} (in Hz) listed in parentheses, if known. [b] Solvent is CD_2Cl_2.

shows resonances at 236.1 (J_{CW} = 112 Hz) and 141.3 ppm ($J_{CW} \approx$ 25 Hz) that can be ascribed to α- and β-carbon atoms in a tungstacyclobutadiene ring by comparison with chemical shifts in other tungstacyclobutadiene complexes listed in Table II. An alternative possibility, a tungstatetrahedrane or η^3-cyclopropenyl complex, can be eliminated on the basis of the fact that chemical shifts in such complexes are typically in the range 70–85 ppm[9] and J_{CW} is too small to be observed. The TIPT ligands in $W(C_3Me_3)(TIPT)_3$ appear to be of two basic types. Broad resonances are observed at 25 °C, and the complex patterns observed in low-temperature spectra suggest that rotation about S–C bonds is slow on the NMR time scale. A question we cannot answer at this point is whether the WC_3 ring is planar or puckered,[10] although the chemical shifts for C_α and C_β would suggest that the WC_3 ring in $W(C_3Me_3)(TIPT)_3$ is one of the planar variety. We conclude from these results that thiolate-substituted tungstacyclobutadiene complexes are observable, stable species, at least in the absence of added donor ligands.

A third informative result is that shown in eq 8. $[Et_3NH][W(CMe)(TIPT)_3Cl]$ is entirely analogous, as far as we can tell, to other complexes of this type. It reacts with zinc chloride as shown in eq 9. These results suggest

$$W(C_3Me_3)Cl_3 + 3TIPTH + 3NEt_3 \xrightarrow[-2Et_3NHCl]{\text{ether, fast}} [Et_3NH][W(CMe)(TIPT)_3Cl] \quad (8)$$

$$[Et_3NH][W(CMe)(TIPT)_3Cl] \xrightarrow[CH_2Cl_2]{ZnCl_2\cdot\text{dioxane}} W(CMe)(TIPT)_3 + [Et_3NH][ZnCl_3] \quad (9)$$

that the tungstacyclobutadiene ring in a thiolate complex is not absolutely stable toward loss of an acetylene to give an alkylidyne complex. We suspect in this case that chloride ion displaces 2-butyne at some point (perhaps in $W(C_3Me_3)(TIPT)_3$) because of the result shown in eq 10.

$$W(C_3Me_3)(TIPT)_3 + Et_3NHCl \xrightarrow{-2\text{-butyne}} \underset{84\%}{[Et_3NH][W(CMe)(TIPT)_3Cl]} \quad (10)$$

(It should be noted that an acetylene can be displaced by donor ligands in other tungstacycles that *are* active metathesis catalysts.[1d]) Note also that $W(CMe)(TIPT)_3$ is another example of a stable complex in which the alkylidyne ligand contains a β proton; $Mo(CPr)(TIPT)_3$ was noted earlier.

The final control experiment consisted of a reaction between a trichloride derivative of an alternative to the metallacyclobutadiene complex, a metallatetrahedrane or η^3-cyclopropenyl complex,[2] and LiTMT (eq 11). This

$$W(C_3\text{-}t\text{-}BuMe_2)Cl_3(py)_2 + 3LiTMT \xrightarrow[-3LiCl]{\text{ether}} \underset{60\%\ \text{isolated}}{W(CMe)(TMT)_3(py)} + \underset{\text{observed in situ}}{W(C\text{-}t\text{-}Bu)(TMT)_3(py)} \quad (11)$$

result suggests that η^3-cyclopropenyl complexes containing three thiolate ligands should not be formed irreversibly when thiolate alkylidyne complexes react with acetylenes, as appears to be the case in some circumstances, e.g. when tricarboxylate alkylidyne complexes react with acetylenes.[9] We cannot say whether an acetylene is lost from a planar tungstacyclobutadiene ring or tungstatetrahedrane system in the course of the reaction shown in eq 11 or whether it would be lost in the (hypothetical) absence of pyridine, but these unknowns do not prevent us from concluding that thiolate-substituted tungstatetrahedrane complexes (*if* they form) are not likely to be dead ends.

Conclusions

We are forced to conclude that thiolate complexes of the type we have prepared here simply do not react fast enough with acetylenes to give the intermediate metallacyclobutadiene complexes necessary for metathesis activity. One possible reason is that thiolates bridge readily to give dimers in which the geometry about each metal is pseudo five-coordinate, perhaps even in the case of the TIPT ligand. The other possible reason is that thiolates simply donate so much electron density to the metal that even unambiguously monomeric $M(CR)(SAr)_3$ complexes would not react readily with an acetylene. Therefore we are in a position to propose that in a broad sense alkoxide ligands are the most successful among C-, N-, O-, or S-based ligands in acetylene metathesis complexes of the type we have discussed here because they are the most electron-withdrawing overall and therefore create a metal center that is electrophilic enough to react with an acetylene.

Experimental Section

General Details. General experimental procedures can be found elsewhere.[1b,c] ^{1}H NMR data are reported in CD_2Cl_2 at ~298 K relative to TMS unless otherwise noted. Only alkylidyne carbon atom chemical shifts in ^{13}C NMR spectra are recorded here (Table I). Typical coupling constants and multiplicities are omitted. H_m refers to meta protons on the arenethiolate ring, Me_o to ortho methyl groups, etc. H_{iso} and Me_{iso} refer to isopropyl group methine and methyl protons (either ortho or para) in TIPT ligands.

Preparation of Compounds. $[Mo(C\text{-}t\text{-}Bu)(TMT)_3]_2$. $Mo(C\text{-}t\text{-}Bu)Cl_3(dme)$[1b] (1.00 g, 2.77 mmol) was added in small portions as a solid to an ether solution (75 mL) of LiTMT (1.31 g, 8.30 mmol) at −30 °C. The solution turned yellow and LiCl precipitated. The mixture was warmed to room temperature over the next 90 min. The solvents were removed in vacuo, and the resulting reddish-yellow residue was extracted with pentane until the extracts were colorless. The extracts were filtered, and the solvents were removed in vacuo to give a yellow solid (1.66 g, 97%) that was virtually pure by ^{1}H NMR. It can be used without further purification for subsequent reactions. An analytical sample was obtained by twice recrystallizing the product from a minimum amount of dichloromethane at −40 °C. Small, bright yellow crystals could be isolated in ~65% yield: ^{1}H NMR (293 K) δ 6.81 (br s, 6 H_m), 2.32 (br s, 18, Me_o) and 2.26 (br s, 9, Me_p), 0.65 (br s, 9, *t*-Bu); ^{1}H NMR (213 K) δ 6.82 (2), 6.73 (1), 6.65 (1), 6.57 (1), and 6.10 (1, all aryl H), 2.58 (3), 2.49 (3), 2.29 (6), 2.22 (6), 2.12 (3), 2.10 (3), and 1.88 (3, all TMT Me groups), 0.23 (s, 9, *t*-Bu). Anal. Calcd for $MoC_{32}H_{42}S_3$: C, 62.11; H, 6.84; S, 15.54. Found: C, 61.60; H, 6.85; S, 15.57.

$[Et_3NH][Mo(C\text{-}t\text{-}Bu)(TMT)_3Cl]$. A solution of 2,4,6-trimethylbenzenethiol (0.25 g, 1.66 mmol) and triethylamine (235 μL, 1.69 mmol) in ether (25 mL) was cooled to −30 °C, and blue $Mo(C\text{-}t\text{-}Bu)Cl_3(dme)$ (0.20 g, 0.55 mmol) was added in small

---

[9] See, for example: Schrock, R. R.; Murdzek, J. S.; Freudenberger, J. H.; Churchill, M. R.; Ziller, J. W. *Organometallics* **1986**, *5*, 25.

[10] Churchill, M. R.; Ziller, J. W.; McCullough, L.; Pedersen, S. F.; Schrock, R. R. *Organometallics* **1983**, *2*, 1046.

portions as a solid. The solution turned yellow and then green as Et_3NHCl precipitated. The mixture was allowed to warm to room temperature. After 2 h the mixture was filtered through Celite, and the filtrate was evaporated to dryness in vacuo. The residue was recrystallized from a minimum amount of ether at −40 °C to give the product as yellow crystals (0.35 g, 85%) in two crops: ^1H NMR δ 9.80 (br, 1, Et_3NH), 6.89 (s, 6, H_m), 3.04 (q, 6, $HN(CH_2CH_3)_3$), 2.41 (br s, 18, TMT Me groups), 2.28 (br s, 9, TMT Me groups), 1.28 (t, 9, $HN(CH_2CH_3)_3$), 0.37 (br s, 9, MoC-*t*-Bu); ^1H NMR (253 K) δ 9.69 (br s, 1, Et_3NH), 6.88 (s, 6, H_m), 3.03 (q, 6, $HN(CH_2CH_3)_3$), 2.42, 2.38, and 2.35 (s, 6 each, TMT Me group), 2.30 (s, 3, TMT Me group), 2.26 (s, 6, TMT Me group), 1.25 (t, $HN(CH_2CH_3)_3$), 0.31 (s, 9, MoC-*t*-Bu).

Mo(C-*t*-Bu)(TIPT)$_3$. Mo(C-*t*-Bu)Cl_3(dme) (0.50 g, 1.38 mmol) was added in small portions as a solid to an ether solution (75 mL) of LiTIPT (1.01 g, 4.15 mmol) at −30 °C. The mixture immediately turned yellow. It was warmed to room temperature, and the solvent was removed in vacuo. The reddish yellow residue was extracted with pentane until the extracts were colorless. The extracts were filtered through Celite and then evaporated to dryness in vacuo. The orange-yellow residue thus obtained was virtually pure Mo(C-*t*-Bu)(TIPT)$_3$ by ^1H NMR spectroscopy. It can be used without further purification for subsequent reactions. An analytical sample was obtained by twice recrystallizing the product from a minimum amount of ether and pentane (2:1) at −40 °C: ^1H NMR δ 6.96 (s, 6, H_m), 3.37 (sept, 6, H_{iso}), 2.87 (sept, 3, H_{iso}), 1.24 (d, 18, Me_{iso}), 1.09 (d, 36, Me_{iso}), 1.01 (s, 9, MoC-*t*-Bu). Anal. Calcd for $MoC_{50}H_{78}S_3$: C, 68.93; H, 9.02. Found: C, 68.73; H, 9.40.

[Et_3NH][W(C-*t*-Bu)(TMT)$_3$Cl]. W(C-*t*-Bu)Cl_3(dme)[5] (0.30 g, 0.67 mmol) was added slowly as a solid to a stirred solution of TMTH (0.31 g, 2.00 mmol) and NEt_3 (280 μL, 2.01 mmol) in ether at −30 °C. The solution turned first green and then yellow. The reaction was warmed to room temperature and stirred for 90 min. Pentane (20 mL) was added to completely precipitate the ammonium salt. The mixture was filtered through Celite, and the filtrate was evaporated to dryness in vacuo to yield the product as a yellow-orange solid (0.53 g, 94%) that was pure by ^1H and ^{13}C NMR spectroscopy. An analytical sample was obtained by recrystallization from a minimum amount of ether at −40 °C: ^1H NMR (293 K) δ 9.41 (br s, 1, Et_3NH), 6.89 (s, 6, H_m), 3.06 (br q, 6, $HN(CH_2CH_3)_3$), 2.49 (s, 12, Me_o), 2.43 (s, 6, Me_o or Me_p), 2.34 (s, 3, Me_p), 2.31 (s, 6, Me_p or Me_o), 1.29 (t, 9, $HN(CH_2CH_3)_3$), 0.25 (s, 9, MoC-*t*-Bu). Anal. Calcd for $WC_{38}H_{58}S_3NCl$: C, 54.05; H, 6.92; Cl, 4.20. Found: C, 54.09; H, 7.36; Cl, 4.57.

[W(C-*t*-Bu)(TMT)$_3$]$_2$. W(C-*t*-Bu)Cl_3(dme) (1.00 g, 2.23 mmol) was added slowly as a solid to a stirred solution (25 mL) of (TMS)TMT (1.50 g, 6.68 mmol) in dichloromethane at −40 °C. The solution slowly turned red and then yellow. It was warmed to room temperature and stirred overnight. By the next day a yellow solid had precipitated. The solvents were removed in vacuo, the yellow residue was redissolved in minimal dichloromethane, and the solution was stored at −40 °C. A yellow powder (1.47 g, 93%) was isolated in two crops: ^1H NMR (C_6D_6, 293 K) δ 6.67 (br s, 6, H_m), 2.63 (br s, 18, Me_o), 2.11 (s, 9, Me_p), 0.64 (br s, 9, WC-*t*-Bu); ^1H NMR (213 K) δ 6.85 (2), 6.76 (1), 6.62 (2), and 6.07 (1) (each a s, aryl H), 2.68 (3), 2.60 (3), 2.36 (3), 2.32 (3), 2.26 (6), 2.17 (6), 1.98 (3) (each a s, Me_o and Me_p in TMT), 0.13 (s, 9, WC-*t*-Bu). Anal. Calcd for $WC_{32}H_{42}S_3$: C, 54.38; H, 5.99. Found: C, 54.33; H, 6.02.

[Et_3NH][W(C-*t*-Bu)(TIPT)$_3$Cl]. W(C-*t*-Bu)Cl_3(dme) (1.00 g, 2.23 mmol) was added slowly as a solid to a dichloromethane solution (30 mL) of TIPTH (1.58 g, 6.68 mmol) and NEt_3 (930 μL, 6.69 mmol) while the solution was stirred at −40 °C. The reaction turned first green and then dark red. It was warmed to room temperature and stirred overnight. The next day pentane (20 mL) was added to precipitate Et_3NHCl. The mixture was filtered through Celite and then evaporated to dryness in vacuo to give an orange-yellow solid (2.31 g, 95%) which was virtually pure product by ^1H and ^{13}C NMR spectroscopy: ^1H NMR (293 K) δ 10.02 (br s, 1, Et_3NH), 7.05 (s, 4, H_m) and 7.00 (s, 2, H_m), 4.00, 3.89, 3.70, and 2.91 (each a sept, 2, H_{iso}), 3.11 (br q, 6, $HN(CH_2CH_3)_3$), 2.99 (sept, 1, H_{iso}), 1.47, 1.45, 1.42, 1.36, 1.35, 1.33, and 1.21 (each a d, 6, Me_{iso}), 1.26 (d, 12, Me_{iso}), 1.17 (t, 9, $HN(CH_2CH_3)_3$), 0.26 (s, 9, WC-*t*-Bu). Anal. Calcd for $WC_{56}H_{94}S_3NCl$: C, 61.32; H, 8.64; Cl, 3.23. Found: C, 60.89; H, 8.81; Cl, 3.41.

W(C-*t*-Bu)(TIPT)$_3$. $ZnCl_2$·dioxane (0.41 g, 1.83 mmol) was added slowly to a solution of [Et_3NH][W(C-*t*-Bu)(TIPT)$_3$Cl] (2.00 g, 1.82 mmol) in 40 mL of dichloromethane stirring at −20 °C. The solution was warmed to room temperature, and after 2 h 20 mL of pentane was added to precipitate the zinc salts. The mixture was filtered through Celite, and the filtrate was evaporated to dryness in vacuo. Recrystallization from a minimum amount of ether at −40 °C yielded 1.66 g (95%) of yellow cubes in three crops: ^1H NMR (293 K) δ 7.02 (s, 6, H_m), 3.40 (sept, 6, H_{iso}), 2.89 (sept, 3, H_{iso}), 1.25 (d, 18, Me_p), 1.13 (d, 36, Me_o), 0.84 (s, 9, WC-*t*-Bu). Anal. Calcd for $WC_{50}H_{78}S_3$: C, 62.62; H, 8.20; S, 10.03. Found: C, 62.83; H, 8.41; S, 10.00.

W(CMe)(TMT)$_3$(py). LiTMT (0.55 g, 3.48 mmol) was suspended in ether (40 mL), and the mixture was cooled to −30 °C. Green W(C_3-*t*-BuMe_2)Cl_3(py)$_2$[2] (0.65 g, 1.15 mmol) was added in small portions as a solid. The mixture turned yellow and then red. As the reaction mixture warmed to room temperature, it lightened to yellow-orange and LiCl precipitated. After 4 h at 25 °C, the solvents were removed in vacuo. The yellow residue was extracted with ether, and the extracts were filtered through Celite. The solvent was removed in vacuo, and the residue was recrystallized from a minimum amount of dichloromethane and ether (3:2) at −40 °C to give yellow, crystalline W(CMe)(TMT)$_3$(py) (0.52 g, 61%) in two crops. A ^1H NMR spectrum (in C_6D_6) of what remained in the mother liquor showed it to be almost exclusively W(C-*t*-Bu)(TMT)$_3$(py); it is too soluble to isolate on this scale: ^1H NMR (293 K) δ 8.89 (br, 2, py), 7.62 (br t, 1, py), 7.09 (br t, 2, py), 6.91 (s, 4, H_m), 6.55 (s, 2, H_m), 2.49 (br s, 12, Me_o), 2.32 (s, 6, Me_o or Me_p), 2.29 (s, 6, Me_o or Me_p), 2.19 (s, 3, Me_p), 2.15 (s, 3, WCMe); ^1H NMR (213 K) δ 8.84 (d, 2, py), 7.60 (t, 1, py), 7.07 (t, 2, py), 6.92 (s, 2, H_m), 6.86 (s, 2, H_m), 6.48 (s, 2, H_m), 2.51 (s, 6, Me_o or Me_p), 2.33 (s, 6, Me_o or Me_p), 2.28 (s, 6, Me_o or Me_p), 2.21 (s, 6, Me_o or Me_p), 2.09 (s, 3, Me_p), 2.04 (s, 3, WCMe). Anal. Calcd for $WC_{34}H_{41}NS_3$: C, 54.91; H, 5.56. Found: C, 55.41; H, 5.54.

Mo(CPr)(TIPT)$_3$. Excess 4-octyne (70 μL, 0.48 mmol) was added to a yellow ether solution (15 mL) of Mo(C-*t*-Bu)[$OCMe_2(CF_3)$]$_3$[1b] (50 mg, 0.09 mmol). After 60 min the solvents were removed in vacuo, leaving Mo(CPr)[$OCMe_2(CF_3)$]$_3$ as a pale yellow solid.[1b] This solid was redissolved in ether (5 mL), and this solution was added dropwise to a solution of LiTIPT (70 mg, 0.29 mmol) in ether (15 mL) that had been cooled to −30 °C. The now orange-red solution was allowed to warm to room temperature. After 2 h the solvent was removed in vacuo. The residue was extracted with pentane, and the extract was filtered through Celite and then evaporated to dryness. The yellow-orange solid thus obtained was virtually pure by ^1H and ^{13}C NMR spectroscopy: ^1H NMR δ 7.02 (s, 6, H_m), 3.52 (sept, 6, H_{iso}), 2.90 (sept, 3, H_{iso}), 2.20 (t, 2, $MoCCH_2CH_2CH_3$), 1.26 (d, 36, Me_{iso}), 1.18 (d, 18, Me_{iso}), 0.78 (sextet, 2, $MoCCH_2CH_2CH_3$), 0.48 (t, 3, $MoCCH_2CH_2CH_3$).

W(C_3Me_3)(TIPT)$_3$. LiTIPT (0.49 g, 2.02 mmol) was dissolved in ether (20 mL), and the solution was stirred at −30 °C. W(C_3Me_3)Cl_3 (0.25 g, 0.67 mmol) was added in small portions as a solid. The solution turned dark red and lithium chloride precipitated. The reaction was allowed to warm to room temperature over the next 2 h and all volatile components were then removed in vacuo. The residue was extracted with pentane, the extracts were filtered through Celite, and the filtrate was evaporated to dryness in vacuo, leaving a red-orange solid. This solid was taken up in dichloromethane-d_2 for ^1H NMR studies (see text) that were sufficient to identify the product.

[Et_3NH][W(CMe)(TIPT)$_3$Cl]. W(C_3Me_3)Cl_3 (0.25 g, 0.67 mmol) was dissolved in ether (20 mL), and the solution was cooled to −30 °C. While the solution was stirred, NEt_3 (281 μL, 2.02 mmol) was added all at once followed by TIPTH (0.48 g, 2.02 mmol) dropwise over a period of several minutes. The solution changed from red to yellow during this period and Et_3NHCl precipitated. The reaction was allowed to warm to room temperature over the next 1.5 h, and 20 mL of pentane was added in order to complete the precipitation of Et_3NHCl. The mixture was filtered through Celite, and the filtrate was evaporated to dryness in vacuo. The residue was recrystallized from a mixture of dichloromethane and pentane (4:1) at −40 °C to yield bright yellow crystals (0.60 g, 84%) in two crops. A procedure involving preparation of W(C_3Me_3)(TIPT)$_3$ as described above followed by addition of 1 equiv of Et_3NHCl in dichloromethane at −30 °C gave

Organometallics **1988,** *7,* 441–448

an identical product upon workup as described here: ^{1}H NMR δ 9.87 (br s, 1, Et_3NH), 7.27 (2), 7.24 (2), and 7.12 (2) (each a s, H_m), 4.67 (br, 2, H_{iso}), 4.40 (sept, 2, H_{iso}), 3.78 (br, 2, H_{iso}), 2.92 (sept, 1, H_{iso}), 2.85 (sept, 2, H_{iso}), 2.49 (s, 3, WCMe), 2.17 (br q, 6, $HN(CH_2CH_3)_3$), 1.80 (12), 1.49 (6), 1.42 (12), 1.31 (6), and 1.22 (18) (each a br d, Me_{iso}), 0.66 (t, 9, $HN(CH_2CH_3)_3$). Anal. Calcd for $WC_{53}H_{88}S_3NCl$: C, 60.35; H, 8.41; Cl, 3.36. Found: C, 60.95; H, 8.66; Cl, 3.03.

W(CMe)(TIPT)$_3$. $[Et_3NH][W(CMe)(TIPT)_3Cl]$ (0.69 g, 0.65 mmol) was dissolved in dichloromethane (20 mL). The reaction was stirred as $ZnCl_2$·dioxane (0.15 g, 0.66 mmol) was added as a solid over 1–2 min. The reaction mixture turned from yellow to dark red over the next 2 h. After 4 h pentane (20 mL) was added in order to precipitate any zinc salts remaining in solution. The resulting mixture was filtered through Celite, and the filtrate was evaporated to dryness in vacuo. The dark red, oily residue was dissolved in a minimum amount of pentane, and the solution was stored at −40 °C. Opaque, yellow-orange crystals (0.29 g, 48%) were isolated in two crops: ^{1}H NMR δ 7.01 (s, 6, H_m), 3.64 (sept, 6, H_{iso}), 2.90 (sept, 3, H_{iso}), 2.36 (s, 3, WCMe), 1.24 (d, 18, H_{iso}), 1.21 (d, 36, H_{iso}). The product was identified by comparison of its NMR spectrum with those of analogues (see above).

Registry No. **3**, 111975-79-2; $[Et_3NH]$[**4** (M = Mo)], 111997-38-7; $[Et_3NH]$[**4** (M = W)], 111997-40-1; LiTMT, 111975-80-5; TMTH, 1541-10-2; LiTIPT, 107847-82-5; (TMS)-TMT, 60253-72-7; Mo(C-*t*-Bu)Cl_3(dme), 98300-84-6; Mo(C-*t*-Bu)$(TIPT)_3$, 111975-81-6; W(C-*t*-Bu)Cl_3(dme), 83416-70-0; [W-(C-*t*-Bu)$(TMT)_3]_2$, 111997-41-2; $[Et_3NH]$[W(C-*t*-Bu)$(TIPT)_3Cl$], 111975-83-8; W(C-*t*-Bu)$(TIPT)_3$, 111975-84-9; W(C_3-*t*-BuMe_2)-Cl_3(py), 91230-72-7; W(CMe)$(TMT)_3$(py), 111975-85-0; Mo(C-Pr)$(TIPT)_3$, 111975-86-1; W$(C_3Me_3)(TIPT)_3$, 111975-87-2; $[Et_3NH][W(CMe)(TIPT)_3Cl]$, 111975-89-4; W(CMe)$(TIPT)_3$, 111975-90-7; Mo(C-*t*-Bu)$[OCMe_2(CF_3)]_3$, 90792-33-9; W-$(C_3Me_3)Cl_3$, 102342-00-7; $ZnCl_2$·dioxane, 16457-66-2; 4-octyne, 1942-45-6.

Systematic Synthesis of Mixed-Metal Clusters via Capping Reactions. Characterization of a Set of Octanuclear Carbido Clusters Involving Rhenium and Various Platinum Metals

Timothy J. Henly and John R. Shapley*

School of Chemical Sciences and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801

Arnold L. Rheingold and Steven J. Geib

Department of Chemistry, University of Delaware, Newark, Delaware 19716

Received July 11, 1987

The cluster $[Re_7C(CO)_{21}]^{3-}$ reacts with a variety of platinum metal based electrophiles to afford the new mixed-metal clusters $[Re_7C(CO)_{21}ML_n]^{2-}$, where ML_n = $Rh(CO)_2$, $Rh(CO)(PPh_3)$, Rh(COD), Ir(COD), $Pd(C_3H_5)$, $Pt(C_4H_7)$, and $Pt(CH_3)_3$. These complexes have been isolated as salts with various large cations and have been characterized by IR (ν_{CO}), ^{1}H NMR, and fast atom bombardment mass spectroscopies. Variable-temperature ^{13}C NMR spectroscopic studies of selected complexes show that each of these compounds adopts a 1,4-bicapped octahedral geometry in solution. This observation is in accord with the solid-state structure of $[PPN]_2[Re_7C(CO)_{21}Pt(C_4H_7)]$, which has been determined by X-ray crystallography. The compound crystallizes in the monoclinic space group $P2_1/n$, with a = 13.412 (5) Å, b = 18.095 (6) Å, c = 20.686 (3) Å, and β = 107.21 (2)°, Z = 2, and the structure has been refined to $R(F)$ = 0.0618 and $R(wF)$ = 0.0688. Cyclic voltammetry studies reveal two oxidation waves for each compound, with $E_{1/2}$ strongly dependent on ML_n.

Introduction

The largest known rhenium carbonyl clusters are $[Re_7C(CO)_{21}]^{3-}$ and $[Re_8C(CO)_{24}]^{2-}$. These complexes were first prepared by Ciani and co-workers, who also showed their structures to consist of an octahedral $[\{Re(CO)_3\}_6C]^{4-}$ core, with one or two additional $Re(CO)_3^+$ caps.[1,2] Previous work in our group has resulted in the direct, high-yield synthesis of either $[Re_7C(CO)_{21}]^{3-}$ or $[Re_8C(CO)_{24}]^{2-}$ by sodium reduction of $Re_2(CO)_{10}$ at 200 °C.[3] Furthermore, we have discovered that $[Re_7C(CO)_{21}]^{3-}$ reacts with $Re_2(CO)_{10}$ to give $[Re_8C(CO)_{24}]^{2-}$, a reaction that can be viewed formally as the capping of one face of $[Re_7C(CO)_{21}]^{3-}$ by a $Re(CO)_3^+$ moiety. Considering the formal relationship between $(\eta^5\text{-}C_5H_5)Re(CO)_3$ (I) and $[Re_8C(CO)_{24}]^{2-}$ (II) suggests an analogy between $[Re_7C(CO)_{21}]^{3-}$ and $[C_5H_5]^-$. The same type of analogy has been drawn for Hawthorne's dicarbollide anion, $[C_2B_9H_{11}]^{2-}$,[4] and many other carboranes.[5] The Cp^-/Re_7^{3-} relationship suggests that mixed-metal clusters of the type $[Re_7C(CO)_{21}ML_n]^{2-}$ (III) might be broadly accessible.

The capping of a triangular face of a closo polyhedron has been treated theoretically. Mingos[6] has described the capping reaction as a condensation reaction between the

---

(1) Ciani, G.; D'Alfonso, G.; Freni, M.; Romiti, P.; Sironi, A. *J. Chem. Soc., Chem. Commun.* **1982**, 339.

(2) Ciani, G.; D'Alfonso, G.; Freni, M.; Romiti, P.; Sironi, A. *J. Chem. Soc., Chem. Commun.* **1982**, 705.

(3) (a) Hayward, C. M. T. Ph.D. Thesis, University of Illinois, Urbana, IL, 1984. (b) Hayward, C. M. T.; Shapley, J. R. *Organometallics*, following paper in this issue.

(4) Hawthorne, M. F.; Young, D. C.; Andrews, T. D.; Howe, D. V.; Pilling, R. L.; Pitts, A. D.; Reintjes, M.; Warren, L. F.; Wegner, P. A. *J. Am. Chem. Soc.* **1968**, *90*, 879.

(5) Grimes, R. N. In *Compehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 1, Chapter 5.5.

(6) Mingos, D. M. P. *Acc. Chem. Res.* **1984**, *17*, 311.

0276-7333/88/2307-0441$01.50/0