cyclopentadienylindium(I) derivatives will be reported in the near future.

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Supplementary Material Available: Tables of atomic coordinates, thermal parameters, bond lengths, and bond angles (13 pages). Ordering information is given on any current masthead page.

Nonplanar, 6π-Electron Metallacyclic Alkylidene Complexes from Coupling of Coordinated Alkynes and η^2-Iminoacyls on a Tantalum Center

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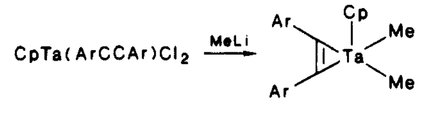
Certain complexes of niobium and tantalum are known to catalyze the polymerization and oligomerization of alkynes, but the details of the mechanism are obscure.[1] We here report the synthesis and transformations of certain alkyne–alkyl complexes of Ta which have bearing on alkyne polymerization catalysis and which lead to an increased understanding of the electronic factors which govern metallacyclic structures.

Treatment of CpTa(ArC≡CAr)Cl_2[2] with 2 equiv of MeLi gives essentially quantitative yields of CpTa (ArC≡CAr)Me_2 (**1**) (Ar = phenyl or *p*-tolyl). The Ta-Me carbons appear at δ 46.3 (q, ${}^1J_{CH}$ = 120 Hz) and the coordinated acetylenic carbons at δ 239.4.

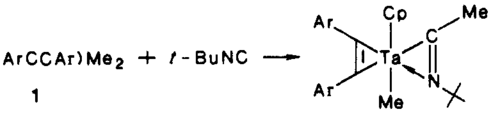


(1)

1

The latter resonance is indicative of 4e⁻ donor acetylenes;[3] therefore, compound **1** is formally a 16-electron complex. Yellow **1** is stable for weeks in the absence of air.

Reaction of **1** with *t*-BuNC gave a nearly quantitative yield of the η^2-iminoacyl complex **2** (eq 2).

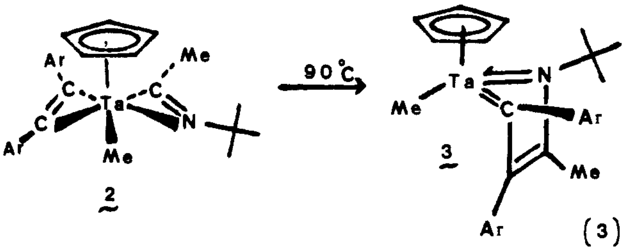


(2)

2

The structure of **2** has been determined crystallographically and the metrical parameters[4] are consonant with a description of the bonding as shown in eq 2. The overall structure is very similar to that of CpMo(RCCR)$_2$L complexes.[5] The ${}^{13}C$ NMR resonance of the iminoacyl carbon occurs at δ 241.1 and the alkyne carbon resonance appears as a single peak at δ 199.7 down to −80 °C. EHMO calculations also suggest a low barrier for end over end rotation of the coordinated alkyne.[6]

Heating a toluene solution of **2** causes the coordinated alkyne and η^2-iminoacyl to couple and the five-membered metallacycle **3** forms quantitatively after 15 h at 90 °C.

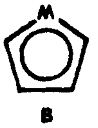


(3)

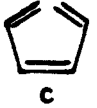
The structure of **3** is quite interesting. The TaC_3N ring is folded 120° (Figure 1) and the Ta—C_α and Ta—N distances in the metallacycle are both 1.98 (1) Å and are commensurate with Ta═C and Ta═N double bonds.[7,8] The C_α—C_β (1.48 (1) Å) and N—C'_β (1.40 (1) Å) bonds are relatively long, while the C_β–C'_β (1.39 (2) Å) distance is short. These distances suggest that the ring structure in **3** is a derivative of a metallacyclopenta*tri*ene (C, see below). This view is supported also by the ${}^{13}C$ NMR spectrum of **3**. The resonance of C_α occurs at δ 231.6 in the range expected for terminal alkylidenes, and the C_β and C'_β resonances are found at δ 95.7 and 121.5.

Thorn and Hoffmann have analyzed the electronic structure of d^0, d^6, and d^8 MC_4R_4 metallacyclopentadienes, A, and have described the requirements necessary to attain a delocalized or "aromatic" metallacycle, B.[9] Briefly, these requirements are that (1) the metal fragment possess an empty orbital to accept electrons from the π_2 MO of the C_4R_4 fragment and (2) a filled orbital to donate electrons to the empty π^*_3 MO (see below). The net electron transfer from π_2 to π^*_3 decreases the C_α–C_β bond order and increases the C_β–C'_β bond order. At some point, these bond orders become equal and the "delocalized" structure B results. This synergic bonding interaction also results in M═C_α multiple bond character.

A

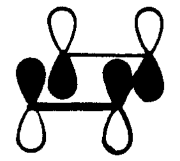


B

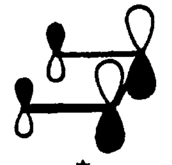


C

D



π_2



π_3^*

The cyclopenta*tri*ene structure C is then seen as an extreme case of the electron redistribution between π_2 and π^*_3 described above. EHMO calculations [10] show that the d^2, CpNb(R)$^+$ fragment has the requisite donor and acceptor orbitals and, of course, the $C_3NR_4^{1-}$ fragment is isoelectronic and isolobal with the $C_4R_4^{2-}$ fragments discussed by Thorn and Hoffman.[9]

The electronic driving force for the ring folding observed in **3** has been analyzed with the EHMO method.[10] The largest effect seems to be the relief of M···C_β *anti*bonding interactions when the ring is folded. In the bent configuration, the M–C_β overlap population is essentially zero but is −0.12 in the planar configuration. Other examples of bent, 6π-electron metallacycles are

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(4) Some relevant distances: C═C, 1.30 (1); C═N, 1.25 (1); Ta—C-(iminoacyl), 2.10 (1); Ta—N, 2.12 (1); Ta—Me, 2.26 (1) Å. Complete tables of bond distances etc. are included in the supplementary material.

(5) Mead, K. A.; Morgan, H.; Woodward, P. *J. Chem. Soc., Dalton Trans.* *1983*, 271.

(6) EHMO calculations were performed on the Nb analogues. For related calculations, see: (a) Kreissel, F. R.; Sieber, W. J.; Hofmann, P.; Riedle, J.; Wolfgruber, M. *Organometallics* **1985**, *4*, 788. (b) Schilling, B. E. R.; Hoffmann, R.; Faller, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 592.

(7) Ta═C distances range from 1.89 (3) to 2.07 (1) Å (av = 2.00 [8] Å): (a) Schrock, R. R.; Messerle, L. W.; Wood, C. D.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1978**, *100*, 3793. (b) Guggenberger, L. J.; Schrock, R. R. *Ibid.* **1975**, *97*, 6578. (c) Churchill, M. R.; Hollander, F. J.; Schrock, R. R. *Ibid.* **1978**, *100*, 647. (d) Chamberlain, L.; Rothwell, I. P.; Huffman, J. C. *Ibid.* **1982**, *104*, 7338.

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(10) Curtis, M. D., unpublished results.

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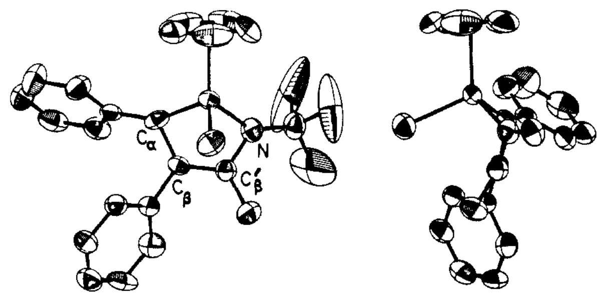

Figure 1. ORTEP plots (50% probability ellipsoids) of CpTa(Me)(CPhCPhCMeN *t*-Bu) (3). Bond distances: Ta–C_α, 1.98 (1); Ta–N, 1.98 (1); C_α–C_β, 1.48 (2); C_β–C'_β, 1.39 (2); C'_β–N, 1.40 (1) Å. The methyl groups in the *tert*-butyl group have been deleted from the drawing on the right.

$(ArO)_2\overline{Zr(NRCHCHN}R)$[11] and $Cp^*_2\overline{Zr(OCHCHO})$.[12] The ring folding in the latter has also been interpreted with the EHMO model.[12]

Compounds 1–3 have the requisite structures to be acetylene polymerization catalysts.[13] In fact, terminal acetylenes are readily polymerized by these and related compounds and these results will be communicated in due course.[14]

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Supplementary Material Available: Table of ^1H and ^{13}C NMR spectral data for 1–3, tables of crystal and data collection statistics, fractional atomic coordinates, thermal parameters, bond distances, and bond angles, and ORTEP drawings for 2 and 3 (13 pages). Ordering information is given on any current masthead page.

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On the Mechanism of the Homogeneous Catalytic Hydrogenation Using Anion-Promoted Metal Clusters

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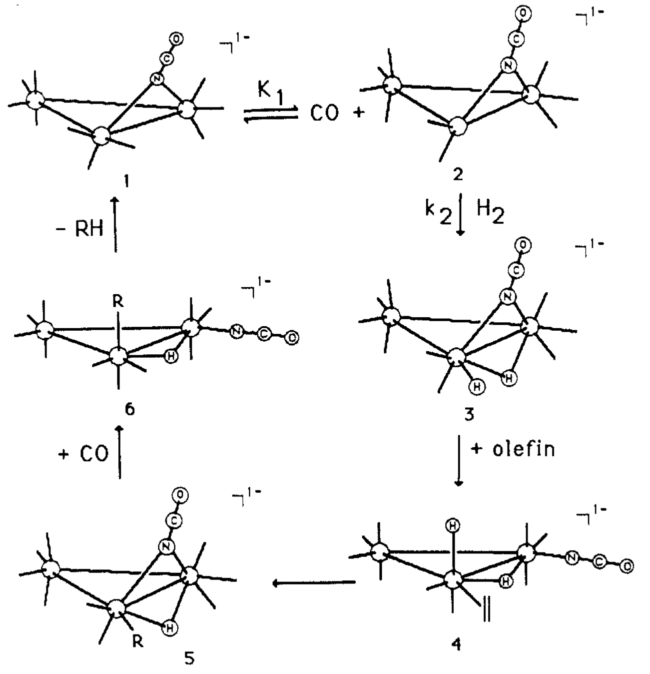
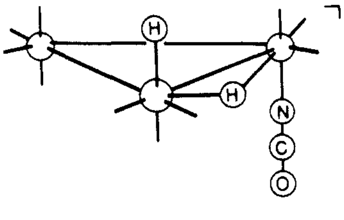
We recently reported[2] that anions, in particular isocyanate, were effective in converting normally unreactive $Ru_3(CO)_{12}$ into an active catalyst (5–6 turnovers/min under ambient conditions) for alkene hydrogenation. While both spectroscopic and kinetic evidence supported a catalytic cycle involving an intact ruthenium triangle, no intermediates were isolated. With the hope of isolating such species, we turned to the osmium system and have found a rich chemistry that is reported here.

The scenario posed in Scheme I was based upon the earlier studies which established that $[Ru_3(NCO)(CO)_{10}]^{1-}$ was the active catalyst. Using the compounds formulated in this scheme as targets, we initially synthesized the anionic osmium isocyanato clusters using the same reaction found successful in the ruthenium chemistry.[3] $PPN(N_3)$ (where PPN = bis(triphenylphosphine)iminium cation) quantitatively converts $Os_3(CO)_{12}$ to $PPN[Os_3(NCO)(CO)_{11}]$[4] in THF, and the infrared spectrum of this compound indicated all the ligands were terminally bound to the metals. During 3.5 h in refluxing THF, $[Os_3(NCO)(CO)_{11}]^{1-}$ smoothly converted into $[Os_3(NCO)(CO)_{10}]^{1-}$ (**1** in Scheme I). While this cluster could not be isolated as crystalline material, the infrared spectrum in the carbonyl region was nearly superimposable upon that of the structurally characterized cluster $[Os_3(NO)(CO)_{10}]^{1-}$.[5] The shift from 2248 to 2217 cm^{-1} for the isocyanate stretch in going from $[Os_3(NCO)(CO)_{11}]^{1-}$ to $[Os_3(NCO)(CO)_{10}]^{1-}$ is characteristic for the conversion of a terminal to bridging isocyanate ligand.[3] The only difference between $[Os_3(NCO)(CO)_{10}]^{1-}$ and the ruthenium analogue is the absence of the semitriply bridging carbonyl.

Scheme I



Molecular hydrogen reacts with $[Os_3(NCO)(CO)_{11}]^{1-}$ in a sealed tube at 50 psig and 52 °C to form $[H_2Os_3(NCO)(CO)_{10}]^{1-}$.[6] The independent synthesis of this cluster involves the straightforward extension of the known chemistry of $H_2Os_3(CO)_{10}$.[7-10] This neutral, unsaturated cluster reacts with PPN(NCO) to give $[H_2Os_3(NCO)(CO)_{10}]^{1-}$ whose structure[11] shown below is similar



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[4] Characterization of $PPN[Os_3(NCO)(CO)_{11}]$. Anal. Calcd: C, 39.51; H, 2.07; N, 1.92. Found: C, 39.55; H, 2.16; N, 1.83. IR(THF): ν_{NCO} 2248 cm^{-1} (br), ν_{CO} 2098 w, 2043 m, 2031 s, 2006 vs, 1994 m (sh), 1984 w (sh), 1961 m, 1938 w (sh) cm^{-1}.

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[6] Characterization of $PPN[H_2Os_3(NCO)(CO)_{10}]$. Anal. Calcd.: C, 39.39; H, 2.25; N, 1.95. Found: C, 39.53; H, 2.30; N, 1.88. IR(THF): ν_{NCO} 2252 cm^{-1} (br), ν_{CO} 2091 w, 2056 s, 2041 m, 2009 vs, 1994 vs, 1963 m, 1945 w, 1928 w (sh) cm^{-1}. ^1H NMR ($CDCl_3$): δ (−76 °C) −10.16 (d, *J* = 3.75 Hz, 1 H), −16.61 (d, *J* = 3.75 Hz, 1 H). 17% of a second isomer is observable in the ^1H NMR spectrum: (23 °C) −8.27 (s, 1 H), −16.20 (s, 1 H). Interconversion between the isomers is slow on the NMR time scale but fast on the laboratory time scale.

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