LaC_{60} ionization threshold and electron affinity should, however, be of great help for checking this calculation and maybe resolve the question concerning the LaC_{60} structure.

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Pentadienyl Chemistry of Niobium and Tantalum: Surprising Differences and New Diene and Dienyl Coordination Patterns

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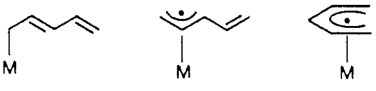
Recently there has been a significant increase in the attention being given to metal-pentadienyl chemistry.[2] Much of this has arisen from the realization that pentadienyl ligands may adopt a variety of bonding modes, e.g., η^1, η^3, or η^5 (I-III),[3] and that they readily partake in catalytic, "naked metal", and coupling reactions,[4] even though the pentadienyl ligand may bond more strongly than cyclopentadienyl.[4e,5]



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A part of our efforts in this area has focused on complexes that simultaneously contain both pentadienyl and cyclopentadienyl ligands, so that the bonding and reactivity patterns of the two may be directly compared. Some of our results for various "half-open metallocenes" have already been described.[4e,6] Herein we report our initial results on related chemistry of niobium and tantalum, including the observation of dramatic differences between the behaviors of these two similar metals,[7] the first definitive demonstration of simultaneous *cis*- and *trans*-η^4-diene coordination to a metal center[8] (η^4-trans coordination being rare in any event[9]), and the first observation of a new η^3-pentadienyl mode of coordination.

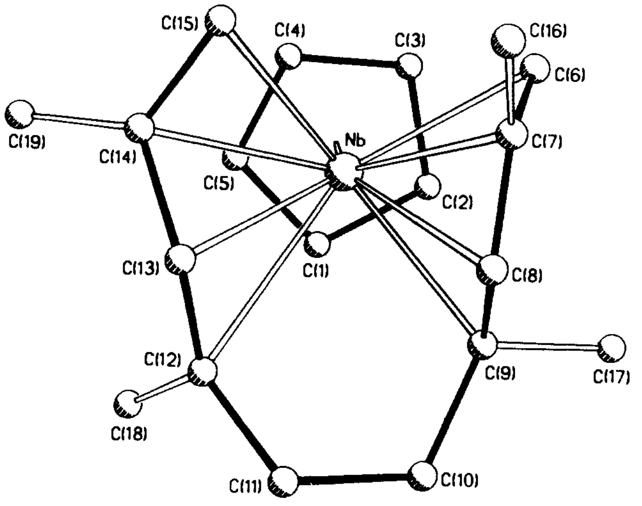

Figure 1. Perspective view and numbering scheme for $Nb(C_5H_5)(\eta^8\text{-}C_{14}H_{22})$. Pertinent bonding distances (Å): Nb–C (Cp, av) = 2.38 (1), C(9)–C(10) = 1.48 (2), C(10)–C(11) = 1.54 (2), C(11)–C(12) = 1.48 (2).

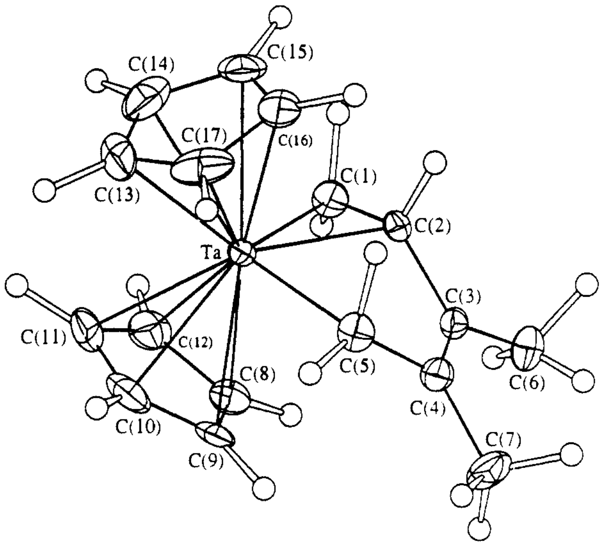

Figure 2. Perspective view and numbering scheme for $Ta(C_5H_5)_2(\eta^3\text{-}2,3\text{-}C_7H_{11})$. Pertinent bonding distances (Å): Ta–C (Cp, av) = 2.416, Ta–C(1) = 2.302 (4), Ta–C(2) = 2.245 (4), Ta–C(5) = 2.296 (5), C(1)–C(2) = 1.434 (6), C(2)–C(3) = 1.499 (5), C(3)–C(4) = 1.333 (6), C(4)–C(5) = 1.517 (6), C(3)–C(6) = 1.497 (6), C(4)–C(7) = 1.512 (6).

The reaction of $Nb(C_5H_5)Cl_4$[10] with 4 equiv of $K(2,4\text{-}C_7H_{11})$[11] (C_7H_{11} = dimethylpentadienyl) initially yields a metastable product, apparently $Nb(C_5H_5)(2,4\text{-}C_7H_{11})_2$ from spectroscopic data,[12] which subsequently undergoes an intramolecular coupling reaction, yielding an unusual $Nb(C_5H_5)(\eta^8\text{-}C_{14}H_{22})$ ($C_{14}H_{22}$ = 2,4,7,9-tetramethyl-1,3,7,9-decatetraene) complex.[13] While other $Nb(C_5H_5)(\eta^4\text{-diene})_2$ species have been reported,[9b] structural

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(12) The orange Nb(III) complex may be isolated at low temperatures. It possesses a ν(C=C) of 1606 cm^{-1} and four CH_2 resonances in the ^{13}C NMR spectrum, three in the usual region (41.8, 45.8, and 46.6 ppm) and the fourth at 114.1 ppm (all C–H couplings in the range of 148–155 Hz).

(13) Synthetic, spectroscopic, and analytical details for new compounds are included in the Supplementary Material. Yields for the niobium reactions ranged from 55–62%, compared to 20–30% for tantalum.

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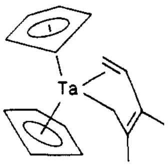
studies to date have thus far only revealed diene units coordinated in the usual cis fashion, whereas a diffraction study for Nb(C_5H_5)(η^8-$C_{14}H_{22}$) has revealed that one of the diene units is present in the trans form (Figure 1).[8,14] Such coordination had previously been observed only for Zr(C_5H_5)$_2$(η^4-diene) and Mo(C_5H_5)(NO)(η^4-diene) complexes,[9] although we have also found trans-diene coordination in Ru(η^4-diene)(acac)$_2$ complexes.[15] The niobium complex now provides the first opportunity to compare simultaneous η^4-*cis*- and η^4-*trans*-diene coordination modes to a single metal center. While the complex might appear to be a Nb(I) compound, it is quite common for diene coordination in "low valent" early metal complexes to possess significant butenediyl character (IV), as opposed to the normal diene form (V).[8] Such coordination (IV) is generally manifested by a long–short–long carbon backbone and a short–long–long–short series of metal–carbon distances. In Nb(C_5H_5)(η^8-$C_{14}H_{22}$), it is the η^4-*cis*-diene portion which engages in butenediyl coordination (having C–C distances of 1.55 (3), 1.32 (2), and 1.52 (2) Å, and Nb–C distances of 2.317 (14), 2.590 (20), 2.570 (15), and 2.366 (18) Å), while the trans form engages in more of a diene coordination (having C–C distances of 1.37 (2), 1.47 (2), and 1.41 (2) Å and Nb–C distances of 2.630 (15), 2.349 (16), 2.304 (15), and 2.363 (12) Å).[16] The greater favorability for the *cis*-diene to engage in butenediyl coordination is in accord with results on the zirconium and molybdenum species and agrees with theoretical studies indicating that the η^4-*trans*-diene coordination is favored when the ligand → metal donor interaction is dominant.[17]

IV

V

In marked contrast, related reactions for Ta(C_5H_5)Cl_4 lead to Ta(C_5H_5)$_2$(pentadienyl) (pentadienyl = 2,3-C_7H_{11}, 2,4-C_7H_{11}) complexes. While the existence of M(C_5H_5)$_2$(η^3-allyl) compounds[18] suggests that analogous M(C_5H_5)$_2$(η^3-pentadienyl) complexes should exist (M = Nb, Ta), spectroscopic features of the Ta(C_5H_5)$_2$(pentadienyl) complexes were not in accord with such a formulation. Notably, a low value of $J_{^{13}C-H}$ (123 Hz) was observed for a terminal dienyl carbon atom, although a reasonable C–C stretching frequency for the free double bond was observed, 1607 cm^{-1}.

A single crystal diffraction study for Ta(C_5H_5)$_2$(2,3-C_7H_{11}) revealed that η^3 coordination by the dienyl fragment was indeed present[14] but involved localized tantalum-alkyl and tantalum-olefin coordination,[19] as in VI, which is an entirely new mode of η^3-dienyl coordination. As a significant input of energy should be needed to convert a delocalized allyl anion to localized alkyl anion and olefin units, the avoidance of η^3-allyl coordination suggests that the Ta(C_5H_5)$_2$ coordination sphere has a strong preference for the more localized, in-plane interactions. Interestingly, however, variable temperature NMR studies for Ta(C_5H_5)$_2$(2,4-C_7H_{11}) reveal that the two ends of the C_7H_{11} ligand may become equivalent, with $\Delta G^‡$ = 10.7 ± 0.2 kcal/mol. Similarly the two C_5H_5 ligands may become equivalent, with $\Delta G^‡$ = 10.4 ± 0.2 kcal/mol. For Ta(C_5H_5)$_2$(2,3-C_7H_{11}), the two C_5H_5 ligand resonances were not observed to undergo coalescence, perhaps an indication that the 2,4-C_7H_{11} group adopts more of a U than S (sickle) conformation. For the former complex, it is not clear whether the intermediate in the equilibration is a 16-electron species such as Ta(C_5H_5)$_2$(η^1-2,4-C_7H_{11}) (bound through the central pentadienyl carbon atom) or an 18-electron Ta(η^5-C_5H_5)(η^3-C_5H_5)(η^5-2,4-C_7H_{11}) species.



VI

The above results reveal some unexpected and subtle differences in favorabilities for niobium- and tantalum-dienyl bonding. The products observed in both reactions are each unusual in themselves. It is first clear that *trans*-η^4-diene coordination should be significantly more common than previously expected, even occurring for late metals. Additionally, the pentadienyl ligands have now revealed a new mode of η^3-coordination, one which demonstrates that η^3-dienyl bonding has available to it a dimension and versatility unknown for its η^3-allyl analogues.

Acknowledgment. R.D.E. is grateful to the NSF for support of this work through grants and a creativity award.

Supplementary Material Available: Synthetic and characterization details for the complexes described herein as well as tables of X-ray data collection parameters and atomic and bonding parameters (24 pages); tables of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

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(14) Crystals of Nb(C_5H_5)($C_{14}H_{22}$) are orthorhombic, space group *Pcc*2, with $Z = 4$ and $a = 14.061$ (3) Å, $b = 14.273$ (3) Å, $c = 8.045$ (1) Å. Departures from mirror plane symmetry eliminate the space group *Pccm*. Data were collected at the University of Delaware out to 55° in 2θ, leading to 1621 unique, observed ($F_o > 3\sigma(F_o)$) reflections. Problems were encountered in the structure refinement, possibly due to the pseudo-mirror plane symmetry. Final discrepancy indices of $R = 0.073$ and $R_w = 0.088$ were obtained. For Ta(C_5H_5)$_2$(2,3-C_7H_{11}), a monoclinic space group ($P2_1/c$) was found, with $a = 7.887$ (2) Å, $b = 14.433$ (3) Å, $c = 12.645$ (3) Å, and $\beta = 97.93$ (2)°, for $Z = 4$. Data were collected at the University of Utah out to $2\theta = 51°$, leading to 2034 unique, observed ($I > 3\sigma(I)$) reflections. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were placed in the positions indicated by a difference Fourier map. Final discrepancy indices of $R = 0.034$ and $R_w = 0.038$ were obtained.

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Synthesis and Structure of *closo*-$Sn_9Cr(CO)_3{}^{4-}$: The First Member in a New Class of Polyhedral Clusters

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The development of metallaborane and metallacarborane chemistry during the past 20 years has provided the chemical community with some of the most interesting and diverse molecular clusters known.[1] Incorporation of transition metals into the later main-group clusters, such as the stannides [$Sn_9{}^{4-}$, $Sn_5{}^{2-}$],[2,3] plumbides [$Pb_5{}^{2-}$],[3] antimonides [$Sb_7{}^{3-}$],[4] and arsenides [$As_7{}^{3-}$, $As_{11}{}^{3-}$, $As_{22}{}^{4-}$],[5-7] has received much less attention but should prove

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(1) For review, see: *Comprehensive Organometallic Chemistry-Vol 1*; Wilkinson, G.; Stone, F. G. A.; Abel, E. W., Eds.; Pergamon Press: Oxford, England, 1982; pp 459–542, and references therein.

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