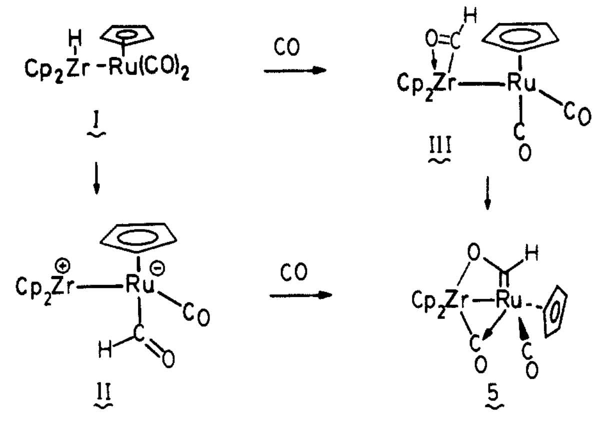
coupling to the α-methylene protons. In the IR spectrum of **4**, bands were observed at 1909 cm^{-1} for the terminal CO, at 1704 cm^{-1} for the semibridging CO, and at 1380 cm^{-1} for the C–O stretch of the zirconoxycarbene.

When the reaction of **2** with ^{13}CO was monitored by ^{13}C NMR, the isotopic label initially appeared only at the carbene carbon of **4**. This observation is consistent with initial insertion of CO into the $Zr-CH_2$ bond, to form an η^2-acyl zirconium intermediate, followed by rapid transfer of the very electrophilic η^2-acyl carbon to the electron-rich ruthenium. Such acyl transfers have been observed before in Zr/Mo systems^5 and may be a general phenomenon in early/late heterobimetallic compounds.

When the CO product **3** was reacted with H_2 (700 mm) at room temperature in THF, the hydrido-zirconoxycarbene complex **5** was obtained ($t_{1/2} \simeq 40$ min). No intermediates were observed by ^1H NMR in THF-d_8. The structure of **5** is very similar to that of **4** and was established by spectroscopy. **5** does not possess a plane of symmetry and consequently three Cp resonances are seen in the ^1H NMR at δ 5.78, 5.40, and 5.39. The ruthenium-bound Cp ligand arises from hydrogenolysis of the $Zr-C_5H_4$ bond. The hydrogen attached to the Ru-bound zirconoxycarbene carbon (or Zr complexed ruthenium formyl) appears at δ 14.05. The IR spectrum of **5** has bands at 1930 cm^{-1} for the terminal Ru–CO, at 1740 cm^{-1} for the semibridging Zr–CO, and at 1350 cm^{-1} for the C–O stretch of the zirconoxy carbene unit. The correspondence between the IR spectra of **4** and **5** indicates that these complexes have the same functional groups. **5** has only limited stability in solution and decomposes slowly at room temperature to a complex mixture of products. **5** was isolated as a slightly impure red solid that slowly decomposes at ambient temperature.

Earlier ^{13}CO exchange studies on **3** demonstrated that rapid CO dissociation from Zr occurs to generate a reactive intermediate^2 which has a Zr-based orbital available for interaction with H_2. We suggest that reaction of this intermediate with H_2 leads to hydrogenolysis of the strained $Zr-C_5H_4$ bond and formation of zirconium hydride intermediate I. This strained $Zr-C_5H_4$ bond is also cleaved by $Cp(CO)_2RuH^2$ and by *t*-BuOH;^{6} hydrogenolysis of Zr–C bonds has been observed previously.^{7} There are two plausible routes from I to **5**. First, addition of the Zr–H to a ruthenium carbonyl^8 could produce ruthenium formyl complex II which could readd CO to Zr to produce **5**. Alternatively, CO could coordinate to I at Zr and insert into the Zr–H bond to produce the η^2-formyl zircononium complex III. Formyl migration to ruthenium as suggested for the formation of **4** could produce **5**. Studies utilizing selectively labeled **3** are in progress to distinguish these alternatives.



It should be noted that reaction of $Cp_2Zr[Ru(CO)_2Cp]_2$ (**1**) with CO and then with H_2 resulted in a net cleavage of a Zr–Ru bond by H_2 and in the formation of the late-transition-metal hydride $Cp(CO)_2RuH$ and of the early-transition-metal hydride intermediate $Cp_2Zr(H)Ru(CO)_2Cp$ (I).

Acknowledgment. Support from the Department of Energy, Division of Basic Energy Sciences, is gratefully acknowledged.

Supplementary Material Available: X-ray crystal data for **4** (28 pages). Ordering information is given on any current masthead page.

---

(5) Longato, B.; Norton, J. R.; Huffman, J. C.; Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 209. Marsella, J. A.; Huffman, J. C.; Caulton, K. G.; Longato, B.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 6360.

(6) Casey, C. P.; Palermo, R. E., unpublished results.

(7) Gell, K. I.; Schwartz, J. *J. Am. Chem. Soc.* **1978**, *100*, 3246.

(8) Intermolecular addition of a zirconium hydride to coordinated CO has been reported. Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1981**, *103*, 2650. Wolczanski, P. T.; Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 218. Barger, P. T.; Bercaw, J. E. *Organometallics*, **1984**, *3*, 278. Barger, P. T.; Santarsiero, B. D.; Armantrout, J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 5178.

Molecular Orbital Calculations on the Th–Ni Interaction in $Th(\eta^5-C_5H_5)_2(\mu-PH_2)_2Ni(CO)_2$

J. V. Ortiz

Department of Chemistry, University of New Mexico
Albuquerque, New Mexico 87131

Received September 10, 1985

Organometallic chemists continue to search for new types of bonding and the relatively unexplored chemistry of the f-block elements^1 presents inviting possibilities. Stimulated by the recent observation^2 of a short Th–Ni separation in $Th(\eta^5-C_5(CH_3)_5)_2(\mu-PPh_2)_2Ni(CO)_2$, the following extended Hückel^3 calculations seek to clarify the nature of the proposed metal–metal interaction.

If one considers the central ThP_2Ni quadrilateral (Figure 1) with the average observed Th–P and Ni–P bond lengths, it is possible to vary the Th–Ni distance by changing the Th–P–Ni angle. (C_{2v} symmetry is maintained in these calculations on $Th(\eta^5-C_5H_5)_2(\mu-PH_2)_2Ni(CO)_2$; the structures of the $(C_5H_5)_2Th$ and $Ni(CO)_2$ fragments are also held constant.) Two structural extremes are now defined. The first has the experimental Th–Ni separation of 3.206 Å while the second takes 3.70 Å for the same quantity. This latter figure arises from an ionic model assumption in which metal atom radii are summed.^{2} Th–P–Ni angles range from 76° to 93° and the P–P distance from 3.84 to 3.41 Å as the Th–Ni separation is increased.

At first glance, the plot of reduced atomic overlap populations (see Figure 2) for this distortion seems disappointing, since the Th–Ni values are negative.^{4} Yet the trend with respect to metal–metal separation is encouraging. Of all the interactions, this one changes the most. Note the relative passivity of Th–P overlap population; apparently there is some geometrical flexibility about the Th. Ni bonding with P is at a maximum when the P–Ni–P angle is near 110°. Of course, P–P overlap populations are indicative of lone pair repulsions and grow more negative as the P–P distance decreases.

Now let the molecule be divided into two fragments: $Cp_2Th(PH_2)_2$ and $Ni(CO)_2$. In terms of the molecular orbitals of these entities, two principal sources of Th–Ni interaction are discernible. First is the filled–filled repulsion between the d-levels of the Ni

---

(1) (a) Marks, T. J. *Science (Washington, D.C.)* **1982**, *217*, 989–997. (b) Marks, T. J., Fischer, R. D., Eds. "Organometallics of the f-Elements"; D. Reidel: Drodrecht, 1979. (c) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51–56. (d) Evans, W. J. *J. Organomet. Chem.* **1983**, *250*, 217–226.

(2) Ritchey, J. M.; Zozulin, A. J.; Wrobleski, D. A.; Ryan, R. R.; Wasserman, H. J.; Moody, D. C.; Paine, R. T. *J. Am. Chem. Soc.* **1985**, *107*, 501–503.

(3) (a) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397–1412. (b) Hoffmann, R.; Lipscomb, W. N. *Ibid.* **1962**, *36*, 2179–2195; **1962**, *37*, 2872–2883. (c) Weighted H_{ij} formulae are employed here: Ammeter, J. H.; Burgi, H. B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686–3692. (d) Th H_{ii} (in eV): –27.07 (6p), –5.99 (5f), –4.95 (6d), –5.31 (7s), –3.22(7p). Slater exponents and contraction coefficients: 3.43 6p; 5.154 (0.5679), 2.468 (0.5936) 5f; 2.756 (0.5789), 1.441 (0.5717) 6d; 1.742 7s; 2.5 (–1.3102), 2.0 (2.035) 7p. The 7p basis function is orthogonal to the 6p basis function.

(4) Reduced atomic overlap populations are indices of the degree of bonding between two atoms. Negative values imply a net antibonding relationship.

0002-7863/86/1508-0550$01.50/0

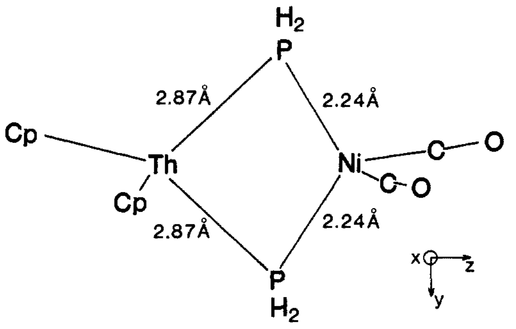


Figure 1. ThP_2Ni quadrilateral with assumed M–P distances and surrounding ligands.

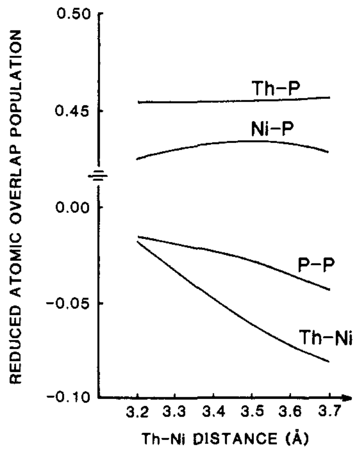


Figure 2. Reduced atomic overlap populations as a function of Th–Ni distance.

fragment and the symmetrized combinations of $3a_1$ and $1b_1$ PH_2 orbitals. The latter are delocalized to some extent onto the Th in a bonding relationship. Therefore, this first interaction is net antibonding between Th and Ni, as well as antibonding between Ni and P. (The overall Ni–P bonding relationship is sustained by acceptance of P lone pair density by empty spd Ni orbitals.) As the geometry is varied, these relationships are conserved.

This brings us to the second source of Th–Ni interaction, between the filled d levels of $Ni(CO)_2$ and the many empty levels of $Cp_2Th(PH_2)_2$ that are centered on Th. Counting the ligands of the latter fragment as anions gives Th^{4+} with a d^0f^0 electron count. Seven empty f orbitals in this C_{2v} fragment give rise to two levels each of b_1, b_2, and a_1 symmetry, plus one a_2 level. Less than 0.4 eV separates the highest (−5.6 eV) from the lowest (−6.0 eV) f-like orbital of $Cp_2Th(PH_2)_2$. About 1 eV higher in energy are four metal-centered spd hybrids of b_2, a_1, a_2, and b_1 symmetry. The largest interaction involves the $Ni(CO)_2$ HOMO, a hybrid of xz and x that points toward the Th in the plane of the Ni fragment's atoms. A similar hybrid ($3b_2$) of xz,x and xz^2 on the Th fragment has an overlap population with the $Ni(CO)_2$ HOMO of 0.054.[5] The $1b_2$ orbital of this fragment is not as diffuse. This mostly xz^2 orbital gives an overlap population of 0.009 with the $Ni(CO)_2$ HOMO; the radial extent of the d Th orbitals is superior for bonding at the distances under consideration here. (The $2b_2$ fragment MO has little bonding influence.) $Ni(CO)_2$'s second HOMO, a mixture of Ni $x^2 - y^2$, z^2, s, and z, has a_1 symmetry. Just above the $3b_2$ orbital of $Cp_2Th(PH_2)_2$ in energy is a z^2,s,z hybrid, $3a_1$, which has an overlap population with $Ni(CO)_2$'s second HOMO of 0.027. As with the previously mentioned b_2 pair of interactions, there is also a stabilization effected by a member of the f orbital set; this time it is the $2a_1$ (z^3) orbital that stabilizes the Ni fragment MO to give an overlap population of 0.005. All of the overlap populations given above obtain for the shortest Th–Ni distance and are reduced by 40–60% when the Th–Ni distance is increased to 3.70 Å. This explains why the Th–Ni curve in Figure 2 ascends with decreasing Th–Ni separation. Letting the z axis define pseudosymmetry implies that the a_1 mixings are σ bonding and that the b_2 mixings are π bonding.

There is a weak donor–acceptor relationship between Ni and Th. This is made possible by the flexibility of the P bridges with respect to bending about the Th as is illustrated by the flatness of the Th–P curve in Figure 2. In an ordinary phosphido-bridged system with no metal–metal bonding, the crucial reduced metal–metal overlap population is negative. The Th center has many unfilled levels which can diminish this antibonding relationship if the Th–Ni distance is reduced.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. Extensive discussions with A. Sattelberger, D. Wrobleski, and R. Ryan of Los Alamos National Laboratory and with R. Paine of the University of New Mexico stimulated this work.

---

[5] The overlap populations cited from here onward are in terms of the basis of fragment MO's of $Cp_2Th(PH_2)_2$ and $Ni(CO)_2$, not in terms of the atomic orbital basis.

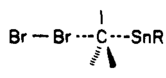
MNDO Study of the Reaction of Tetramethylstannane with Bromine

Michael J. S. Dewar* and Daniel R. Kuhn

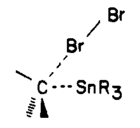
Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712

Received December 20, 1984

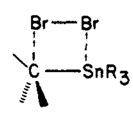
The mechanism of the brominolysis of alkyl tin compounds has been of considerable interest to organometallic chemists primarily due to the observation of stereochemical inversion, as well as retention, at carbon under certain conditions.[1,2] A wide range of mechanistic pathways have been proposed for this reaction, which has been found, in general, to be first order in both Br_2 and the alkyltin.[1,3] These proposed mechanisms included both concerted,[1-3] stepwise,[3] and charge-transfer[4] processes. To rationalize the observed stereochemistry at carbon, three transition states (TS) have been proposed, **1**, below, leading to inversion and **2** and **3**



1



2



3

leading to retention. Note however, that reaction via **3** would be a forbidden process.[5]

---

(1) (a) Fukuto, J. M.; Jensen, F. R. *Acc. Chem. Res.* **1983**, *16*, 177. (b) McGahey, L. F.; Jensen, F. R. *J. Am. Chem. Soc.* **1979**, *101*, 4397. (c) Rham, A.; Peryre, M. *Ibid.* **1977**, *99*, 1673. (d) Jensen, F. R.; Davis, D. D. *Ibid.* **1971**, *93*, 4048. (e) Chambers, R. L.; Jensen, F. R. "Aspects of Mechanism and Organometallic Chemistry"; Brewster, J. H., Ed.; Plenum Press: New York, 1978.

(2) Olszow, H. A.; Kitching, W. *Organometallics* **1984**, *3*, 1676.

(3) (a) Gielen, M.; Frosty, R. *J. Chem. Res., Synop.* **1977**, 214. (b) Gielen, M.; Frosty, R. *J. Chem. Res., Miniprint* **1977**, 2379. (c) Gielen, M. *Acc. Chem. Res.* **1973**, *6*, 198.

(4) Fukuzumi, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 2141.

(5) Slack, D. A.; Baird, M. C. *J. Am. Chem. Soc.* **1976**, *98*, 5539.