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Metal–Metal Bonds Involving the f-Elements. 2. Nature of the Bonding in $(\eta^5\text{-}C_5H_5)_2(I)M\text{–}Ru(\eta^5\text{-}C_5H_5)(CO)_2$ (M = Zr, Th) Complexes[1]

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The chemistry of organoactinide complexes which contain a direct metal–metal bond between an actinide atom and a transition metal is currently of great interest. Recent work at Los Alamos National Laboratory has established two phosphido-bridged complexes of formulation $Cp_2^*Th(\mu\text{-}PPh_2)_2ML_n$ ($Cp^* = \eta^5\text{-}C_5Me_5$; **1**, $ML_n = Ni(CO)_2$; **2**, $ML_n = PtPMe_3$) in which a significant direct interaction between Th and a group 10 metal apparently exists.[3,4] The Th–Ni distance in **1** is 3.206 Å, 0.5 Å shorter than would be expected for a nonbonding interaction. Nonrelativistic extended Hückel calculations predict that a weak donor–acceptor relationship is present between Ni and Th.[5] The Th–Pt bond in **2** is shorter yet, 2.984 Å, which provides even stronger evidence for a direct metal–metal interaction, a conclusion which is further corroborated by ^{31}P NMR spectroscopy.[4] Ab initio calculations were performed on a model of complex **2**, and the authors concluded that a dative donor–acceptor bond was present between the Pt $5d_{x^2-y^2}$ and the Th $6d_{x^2-y^2}$ orbitals.[4] Thus, there is incontrovertible experimental and theoretical evidence that metal–metal interactions are present in **1** and **2**; however, it is difficult to gauge the strengths of these interactions due to the presence of the phosphido bridges.

Marks and co-workers have recently prepared the first two complexes which contain a direct, unsupported bond between an actinide atom and a transition metal by the reaction of $Cp_2^*ThX_2$ with $CpRu(CO)_2Na$ ($Cp = \eta^5\text{-}C_5H_5$).[6] The resultant complexes, $Cp_2^*(X)Th\text{–}RuCp(CO)_2$ (**3**, X = Cl; **4**, X = I); bear a striking resemblance to the transition-metal heterobimetallics $Cp_2(X)Zr\text{–}RuCp(CO)_2$ reported by Casey et al.,[7] and the Th–Ru bond length in **4** (3.028 Å) is very comparable to the Zr–Ru bond length in $Cp_2(OCMe_3)Zr\text{–}RuCp(CO)_2$ (2.910 Å).[7a] The nature of these metal–metal bonds between Ru(0) and (formally) d^0 Zr(IV) or d^0f^0 Th(IV) is a question of great current interest in both organo-early-transition-metal and organo-f-element chemistry. In an effort to better understand the metal–metal bonding in these systems, and to further our comparisons of organoactinide to organo-transition-metal chemistry, we report here Xα–SW molecular orbital calculations[8] with relativistic corrections[9] on the very large and low symmetry (C_s) model complexes $Cp_2(I)M\text{–}RuCp(CO)_2$ (**5**, M = Zr; **6**, M = Th). These are the first quantitative calculations to be reported for such unsupported heterobimetallics.[10]

Table I. Percentage Contributions to the Metal–Metal Bonding Orbitals[a] of $Cp_2(I)Zr\text{–}RuCp(CO)_2$ and $Cp_2(I)Th\text{–}RuCp(CO)_2$

bond	% M	% s	% p	% d	% f
Zr–Ru					
M = Zr	15.3	9.1	7.5	83.4	
M = Ru	72.2	6.6	0.8	92.5	
Th–Ru					
M = Th	15.5	9.7	3.6	71.8	15.5
M = Ru	68.5	6.8	1.8	91.4	

[a] MO 30a′ for Zr–Ru, 31a′ for Th–Ru.

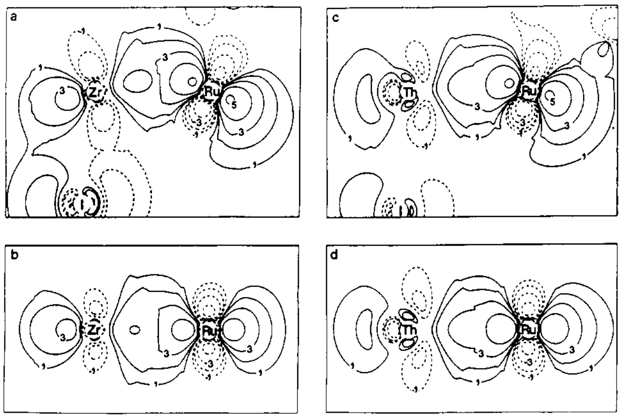

Figure 1. Contour plots of the 30a′ MO of $Cp_2(I)Zr\text{–}RuCp(CO)_2$ (**5**) and the 31a′ MO of $Cp_2(I)Th\text{–}RuCp(CO)_2$ (**6**). Contour values are ±5, ±4, ±3, ±2, ±1 = ±0.32, ±0.16, ±0.08, ±0.04, and ±0.02. (a) Plot of 30a′ MO of **5** in the I–Zr–Ru plane. (b) Plot of 30a′ MO of **5** normal to the I–Zr–Ru plane. (c) Plot of 31a′ MO of **6** in the I–Th–Ru plane. (d) Plot of 31a′ MO of **6** normal to the I–Th–Ru plane.

Not unexpectedly, the early–late transition-metal complex **5** can best be described as containing a donor–acceptor metal–metal bond. The $ZrCp_2I$ fragment can be regarded as a cation which accepts electron density donated from an anionic $RuCp(CO)_2$ fragment. The metal–metal bonding is nearly entirely contained in one MO (the 30a′), and as can be seen in Table I and Figure 1a and 1b, the bond is due to donation of electron density from a mixture of the $4d_{z^2}$ and the $4d_{xz}$ orbitals on Ru into the corresponding $4d_{z^2}$ and $4d_{xz}$ mixture located on Zr.

Due to the similarity between d^0 Zr(IV) and d^0f^0 Th(IV), the Th–Ru bond in **6** might be expected to be similar to the Zr–Ru bond in **5** and also might be best described as a donor–acceptor bond. Indeed, as indicated in Figure 1, the 31a′ metal–metal bonding orbital of **6** is strikingly similar to the 30a′ orbital of **5**. This, of course, raises the question of the relative Th 5f and 6d contributions to the Th–Ru bond. Our previous calculations on organoactinide complexes have shown the metal 6d orbitals to be at least as important as the 5f orbitals for the binding of ligands.[11] In addition, the ab initio calculation[4] on a model of the Th–Pt complex **2** and the extended Hückel calculation[5] on a model of the Th–Ni complex **1** both predict that the metal–metal interaction contains little Th 5f character. Thus, if **6** behaves like either mononuclear Th(IV) complexes or supported heterobimetallics,

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(10) Computational details: Quasirelativistic Xα–SW calculations were carried out in a fashion analogous to our previous calculations on organo-f-element complexes.[11] In order to simplify the calculations, the Cp* ligands of the Th complex **4** were replaced with Cp ligands. The effect of this change has been studied and has been shown to exhibit a small and uniform error which will not affect the conclusions presented here.[12] The structural parameters assumed for the Th complex **6** were taken from ref 6, and those for the Zr complex **5** were taken from the crystal structure of $Cp_2(Cl)Zr\text{–}RuCp(CO)_2$.[7a] The Zr–I bond length in **5** was assumed to be the same as that in Cp_2ZrI_2.[13] Both **5** and **6** were idealized to C_s symmetry.

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it seems likely that the metal–metal bond in the Th–Ru complexes would also contain a relatively small contribution from the Th 5f orbitals. This is most certainly the case as can be seen in Table I, a comparison of the percent contributions in the metal–metal bonding orbitals of **5** and **6**. In both cases the principal contribution is from the d orbitals on all metal centers. The Th 5f orbitals account for only 16% of the total Th contribution to the 31a′ MO of **6** whereas the 6d orbitals account for 72%, comparable to the contribution of the 4d orbitals of Zr to the 30a′ orbital of **5**.

It is also apparent from Table I that the relative distribution of electron density is very similar in both complexes. The Ru atom contributions are nearly identical in **5** and **6**, indicating that the Ru atom is in virtually the same electronic environment in both complexes. Thus, not surprisingly, we find that the metal–metal bond in **6** is best described as a dative donor–acceptor bond formed by electron-pair donation from a formally anionic $RuCp(CO)_2$ fragment to a d^0f^0 Th(IV) atom, entirely analogous to the Zr–Ru bond in **5**.

In conclusion, we have found that the bonding of the $RuCp(CO)_2$ fragment to either a $Cp_2(X)Zr$ or a $Cp^*_2(X)Th$ fragment is not remarkably different from the bonding of other formally anionic ligands (such as halides or alkyls) to the same fragments. In this regard, we feel that $RuCp(CO)_2$ can be regarded as an "organometallic pseudohalide" in these heterobimetallic complexes, a notion which is certainly consistent with the synthetic pathways to the complexes. We believe, therefore, that organoactinide complexes which contain a more covalent metal–metal bond, of which none are yet known, may exhibit very different properties than the heterobimetallics discussed here.

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Comparison of the Relative π-Donor Abilities of Amido and Phosphido Ligands. 1,2-Bis(di-*tert*-butylphosphido)tetrakis(dimethylamido)dimolybdenum and -ditungsten: $1,2\text{-}M_2(P(t\text{-}Bu)_2)_2(NMe_2)_4(M{\equiv}M)$

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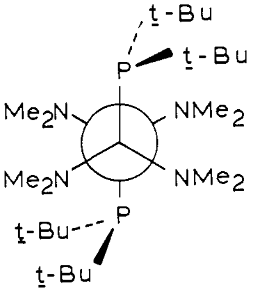
The relative π-donating ability of ligands bonded to transition metals involving first- and second-row elements, e.g., OR vs. SR and NR_2 vs. PR_2, is presently not well understood. The match in orbital energy between the metal and the ligand is generally better with the second-row elements though the shorter M–X σ distances to the first-row elements lead to better π overlap. The effective charge on the metal and the substituents on the ligand are also important variables. In one or two cases, series of compounds, e.g.,[2] (pz)Mo(NO)(X)(Y), are known for a variety of X and Y, including OR and SR, where the properties of a spectator ligand such as ν(NO) vary as a function of X for a given Y. This situation is, however, complicated by the total electron-releasing power (σ + π) of the ligand X. We offer here the first direct comparison of π bonding between phosphido and amido ligands where the two are bonded to the same metal center.

Table I. Summary of Structural Data for $1,2\text{-}M_2(P(t\text{-}Bu)_2)_2(NMe_2)_4$ Compounds[a]

parameter	M = Mo	M = W
M–M	2.2137 (5)	2.3200 (7)
M–N (av)	1.976 (8)	1.97 (1)
M–P	2.477 (1)	2.398 (2)
M–M–N (av)	103.3 (1)	102.5 (25)
M–M–P	104.5 (1)	107.6 (3)
M–N–C(α)[b] (av)	133.0 (4)	132.4 (5)
M–N–C(β)[b] (av)	118.0 (7)	118.4 (9)
C(α)–N–C(β) (av)	108.8 (2)	109.0 (10)
M–P–C(α)	131.4 (1)	135.0 (3)
M–P–C(β)	109.2 (1)	111.9 (8)
C(α)–P–C(β)	108.0 (1)	108.6 (5)

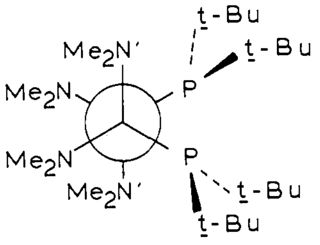
[a] Distances in angstroms and angles in degrees. [b] α = proximal, and β = distal.

Reactions between $1,2\text{-}M_2Cl_2(NMe_2)_4$ (M = Mo and W)[3] and $LiP(t\text{-}Bu)_2$[4] (2 equiv) in tetrahydrofuran (−78 °C followed by warming to room temperature) give red-orange solutions from which the compounds $1,2\text{-}M_2(P(t\text{-}Bu)_2)_2(NMe_2)_4$ (M≡M) have been isolated by evaporation of the solvent, extraction of the residues with hexane, and crystallization.[5] The air-sensitive red (M = Mo) or orange-yellow (M = W) complexes so obtained exist in solution as mixtures of the well-established anti and gauche conformers of compounds of formula $1,2\text{-}M_2X_2(NMe_2)_4$.[6] The molybdenum and tungsten compounds crystallize in anti and gauche conformations, I and II, respectively.[7]



I

M = Mo



II

M = W

Structural parameters for the $M_2N_4P_2$ cores are summarized in Table I. All $M\text{–}NC_2$ units are essentially planar and aligned parallel to the M–M axis, resulting in proximal and distal NMe groups (with respect to the M≡M bond). The $P(t\text{-}Bu)_2$ ligands are aligned similarly, although the $M\text{–}PC_2$ units deviate from planarity. In I rigorous C_i symmetry is crystallographically imposed. In II, which has approximate C_2 symmetry, the $M\text{–}PC_2$ units are bent away from the virtual C_2 axis.

As in other $1,2\text{-}M_2X_2(NMe_2)_4$ structures, the short M–N distances represent M–N double bonds.[8] The Mo–P distance,

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[5] Yields range from 55% to 65% based on M. Dry and oxygen-free solvents and atmospheres were used.

[6] E.g., for X = alkyl or aryl, see: Chisholm, M. H.; Haitko, D. A.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 4046. Chetcuti, M. J.; Chisholm, M. H.; Folting, K.; Haitko, D. A.; Huffman, J. C.; Janos, J. *J. Am. Chem. Soc.* **1983**, *105*, 1163.

[7] Crystal data for $Mo_2(P(t\text{-}Bu)_2)_2(NMe_2)_4$ at −156 °C, $a = 9.763$ (1) Å, $b = 18.210$ (3) Å, $c = 10.031$ (1) Å, $\beta = 117.64$ (1)°, space group $P2_1/n$, $Z = 2$, $d_{calcd} = 1.385$ g cm^{-3}. Using Mo Kα, $6° \leqslant 2\theta \leqslant 50°$, total reflections 3558 with 2525 having $F > 3\sigma(F)$ yielded final residuals $R(F) = 0.024$ and $R_w(F) = 0.027$. $W_2(P(t\text{-}Bu)_2)_2(NMe_2)_4$ at −155 °C, $a = 12.225$ (2) Å, $b = 18.250$ (5) Å, $c = 14.666$ (3) Å, $\beta = 92.03$ (1)°, $Z = 4$, $d_{calcd} = 1.695$ g cm^{-3}, space group $P2_1/n$. Using Mo Kα, $6° < 2\theta < 45°$, total reflections 4535 with $3810 > 3\sigma(F)$ yielded final residuals $R(F) = 0.037$ and $R_w(F) = 0.038$.

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