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.

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-$M_2(P(t\text{-Bu})_2)_2(NMe_2)_4(M\equiv M)$

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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 elec-

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

tron-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.

Reactions between 1,2-$M_2Cl_2(NMe_2)_4$ (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-$M_2(P(t\text{-Bu})_2)_2(NMe_2)_4$ (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-$M_2X_2(NMe_2)_4$.[6] The molybdenum and tungsten compounds crystallize in anti and gauche conformations, I and II, respectively.[7]

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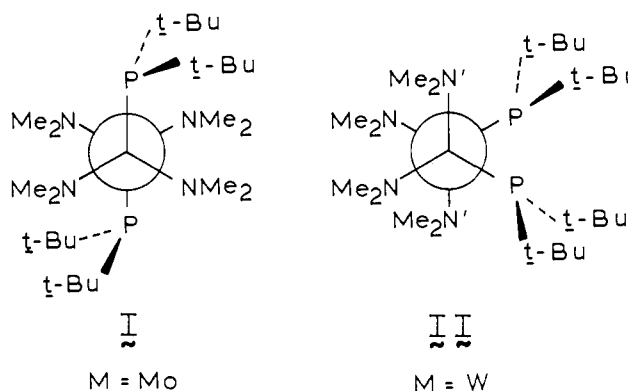
Structural parameters for the $M_2N_4P_2$ cores are summarized in Table I. All M–NC_2 units are essentially planar and aligned parallel to the M–M axis, resulting in proximal and distal NMe groups (with respect to the M≡M bond). The P(t-Bu)$_2$ ligands are aligned similarly, although the M–PC_2 units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

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

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(7) Crystal data for Mo$_2$(P(t-Bu)$_2$)$_2$(NMe$_2$)$_4$ at –156 °C, a = 9.763 (1) Å, b = 18.210 (3) Å, c = 10.031 (1) Å, β = 117.64 (1)°, space group $P2_1/n$, Z = 2, d_{calcd} = 1.385 g cm⁻³. Using Mo Kα, 6° ⩽ 2θ ⩽ 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-Bu)$_2$)$_2$(NMe$_2$)$_4$ at –155 °C, a = 12.225 (2) Å, b = 18.250 (5) Å, c = 14.666 (3) Å, β = 92.03 (1)°, Z = 4, d_{calcd} = 1.695 g cm⁻³, space group $P2_1/n$. Using Mo Kα, 6° < 2θ < 45°, total reflections 4535 with 3810 > 3σ(F) yielded final residuals $R(F)$ = 0.037 and $R_w(F)$ = 0.038.

Table II. Barriers to Rotation, $\Delta G^{\ddagger}_{\mathrm{T}}$ (T_c) (kcal/mol (K)) about M–N and M–P Bonds in *gauche*-1,2-$M_2(P(t\text{-}Bu)_2)_2(NMe_2)_4$

bond	M = Mo	M = W
M–NMe₂	11.5 ± 0.1 (260)	11.3 ± 0.1 (256)
M–N'Me₂	8.2 ± 0.1 (185)	7.5 ± 0.1 (170)
M–P(t-Bu)₂	8.6 ± 0.1 (190)	9.7 ± 0.1 (212)

2.477 (1) Å, is close to that expected for a Mo–P single bond based on the covalent radii r_{Mo} (for (M≡M)⁶⁺) = 1.40 Å⁹ and r_P = 1.10 Å.[10] Furthermore, the geometry at phosphorus is distinctly pyramidal, as evidenced by (i) the sum of the angles about P, 348.5°, and (ii) the deviation of the P atom from the MoC_2 plane of the Mo–PC_2 moiety, 0.41 Å. The W–P distance is shorter than the Mo–P distance by 0.08 Å, and the distortion of the W–PC_2 moiety from planarity is smaller. This is shown in the sum of the angles about P, 355.6°, and the deviation of P from the WC_2 planes, 0.25 Å.

Important structural comparisons can be made as follows. In $Mo(NMe_2)_4$[11] and $Mo(PCy_2)_4$,[12] both of which contain planar (at N and P), 4-electron-donor ($\sigma + \pi$) ligands, the Mo–N and Mo–P distances are 1.926 (6) and 2.265 (2) Å, respectively. A parameter can be calculated, $\Delta = d(Mo\text{–}P) - d(Mo\text{–}N) = 0.339$ Å, to represent the difference in bond lengths of M–NR_2 vs. M–PR_2 double bonds. For 1,2-$M_2(P(t\text{-}Bu)_2)_2(NMe_2)_4$, two NMe_2 and one $P(t\text{-}Bu)_2$ ligand compete for *two* metal acceptor orbitals ($d_{x^2-y^2}$, d_{xy}). The larger Δ values in I, $\Delta = 0.502$ Å, and II, $\Delta = 0.429$ Å, reflect the preference for M←NR_2 π bonding over M←PR_2 π bonding in the mixed-ligand compounds. Of further interest are the M–P distances in $Cp_2Hf(PEt_2)_2$ of 2.682 (1) and 2.488 (1) Å for the pyramidal and planar PR_2 ligands, respectively.[13] Formally, the difference of 0.194 Å corresponds to the difference in M–P single- and double-bond distances. Clearly, the Mo–P bonds in I have little if any π character while the W–P bonds in II have substantially more.[14]

These conclusions based on structural data are supported by the barriers to rotation about M–NMe_2 and M–$P(t\text{-}Bu)_2$ bonds in the 1,2-$M_2(P(t\text{-}Bu)_2)_2(NMe_2)_4$ compounds. Low-temperature ¹H NMR spectra reveal that rotations about M–N and M–P bonds are frozen out on the NMR time scale; NMe and P(t-Bu) proximal and distal resonances are well separated (by 1.9–1.2 and 0.7–0.6 ppm, respectively) as a result of the diamagnetic anisotropy of the (M≡M)⁶⁺ units.[15] Barriers calculated from coalescence temperatures[16] are listed in Table II for the gauche conformers, which predominate in solution: gauche:anti = 2:1 (M = Mo) and 4:1 (M = W). We observe that proximal-to-distal exchange in the $P(t\text{-}Bu)_2$ ligands is more rapid for M = Mo than for M = W, while proximal-to-distal exchange rates for NMe_2 ligands follow the inverse order.[17] If P inversion was also slow at temperatures for which M–N and M–P rotations are frozen out, the observation

of several stereoisomers resulting from the various relative configurations at phosphorus might be expected. Specifically, anti conformers could exist as a mesolike isomer (C_i symmetry as in I) or as an enantiomeric pair having C_2 symmetry. A set of three diastereomers would be expected for gauche conformers, each representing an enantiomeric pair. Our failure to detect such invertomers suggests that inversion at phosphorus in the phosphido ligands is facile[18] and not frozen out on the NMR time scale.

We conclude that amido ligands are stronger π donors than phosphido ligands in 1,2-$M_2(P(t\text{-}Bu)_2)_2(NMe_2)_4$ compounds and that tungsten has a greater propensity to π bond with the PR_2 ligands than molybdenum does. The latter is unlikely due to differences in Mo–P vs. W–P *overlap*, since the covalent radii r_{Mo} and r_W in (M≡M)⁶⁺ compounds are nearly identical,[19] but might be rationalized by orbital energetics. The energy difference in the valence levels for Mo vs. W in (M≡M)⁶⁺ and (M⁴M)⁴⁺ compounds is ca. 0.5 eV, as determined by PES data.[20] The higher energy of tungsten valence orbitals may provide a better energy match with the phosphido 3p orbital, resulting in a stronger π interaction.[21]

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Transition Structures for Hydride Transfers

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Hydride transfers are ubiquitous organic and biochemical reactions.[1-2] The degenerate hydride transfer from methoxide to formaldehyde, a prototype for such reactions, has been observed with labeled compounds in the gas phase by Nibbering et al.[3] We have investigated this reaction theoretically in various geometries and with metal counterions.[4] All structures were optimized with gradient methods, and the stationary points on the potential energy surfaces were characterized by harmonic vibrational frequency calculations, using the GAUSSIAN 80 and GAUSSIAN 82 programs of Pople et al.[5]

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