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cluster, which has the greater freedom in ligand orientation, maintains the shorter M–M bond distance. Especially noteworthy is the latter comparison where even the presence of chloride ligands at the X2 positions of the eight-electron molecular cluster do not induce longer M–M distances than those found in the all-oxide seven-electron polymeric cluster. Additionally, the question of the M–M bonding or antibonding character of the $2a_1$ orbital seems clear, at least in the case of the niobium chloride clusters, where it has been noted that in the six-electron $[Nb_3Cl_{10}(P(C_2H_5)_3)_3]^{-}$[21] molecular cluster the Nb–Nb bond distances (2.976 Å) are considerably longer than those found in either the eight-electron molecular cluster $Nb_3Cl_7(P(CH_3)(C_6H_5)_2)_6$[22] (2.832 Å) or the seven-electron polymeric clusters in α-Nb_3Cl_8 (2.81 Å). The slightly longer distances found in $Nb_3Cl_7(P(CH_3)(C_6H_5)_2)_6$ compared to α-Nb_3Cl_8 may be due to the weak π-acceptor ability of the phosphine ligands.

When sodium intercalates into α-Nb_3Cl_8, only β'-$NaNb_3Cl_8$ is formed, with no phase width or interim phases being observed in the powder pattern. Even when a deficiency of sodium is used, only a mixture of β'-$NaNb_3Cl_8$ and α-Nb_3Cl_8 is observed as product. It may therefore be concluded that the rate-determining step occurs within the initial surface reduction reaction step(s). The apparent high diffusion rate of Na within the lattice is aided by the requirement to form the β'-structure, where cluster layers must shift relative to one another at all van der Waals gaps. This is supported by the observation that the re-formation of α-Nb_3Cl_8 from the deintercalation of β'-$NaNb_3Cl_8$, through the reduction of water or methanol, likewise occurs over several hours and begins within minutes of exposure.

Synthetic procedures for Nb_3Cl_8 employ temperatures of ~800 °C, and the α-phase is the only phase formed.[5a] Synthetic attempts at preparing $NaNb_3Cl_8$ from mixtures of α-Nb_3Cl_8, Nb, and NaCl in sealed ampules at temperatures of 800–1050 °C gave only α-Nb_3Cl_8, Nb_6Cl_{14}, $NaNb_6Cl_{15}$, and/or $Na_4Nb_6Cl_{18}$ as products.[23] The reversible nature of the α-Nb_3Cl_8/β'-$NaNb_3Cl_8$ system further illustrates that the α-form of Nb_3Cl_8 is the most stable (in contrast to Nb_3Br_8 and Nb_3I_8, which are reported to form both α- and β-phases).[5a] When sodium deintercalates from β'-$NaNb_3Cl_8$ at room temperature, if the lattice were to simply contract as the β'-form, the six lone-pair orbitals of the X2 ligands in the B-gap previously directed toward Na^+ (Figure 3a) would continue to point toward one another and would come very close at the 2.969-Å spacing of these anions in Nb_3Cl_8. These orbitals thus repel each other and drive the structural transition back to the α-form, where they now point toward an X3 ligand of a tetrahedral site at a spacing of 3.276 Å. Although the structural relationship of the β'-form to the α'-form is closer than that to the α-form (mechanistic considerations), the non-close-packing of anions at the B-gap of an α'-type (i.e. a trigonal-prismatic site) brings these X2 orbitals in even closer contact than in a β'-structure. Thus, the α'-, β'-, and β-forms all require larger cell dimensions than those achieved in the α-form, and for this reason Nb_3Cl_8 exists with the α-structure. An increased polarizability of the lone-pair orbitals should stabilize the β- or β'-structures in this respect, as is observed for β-Nb_3Br_8 and β-Nb_3I_8.[5a]

The X-ray pattern of β'-$NaNb_3Cl_8$ is observed (with small changes occurring at ~100 and ~200 °C) up to ~400 °C, at which point the phase loses some or all of the Na in the form of NaCl. Intriguingly, the powder diagram of the product closely resembles the theoretical diagram expected for a γ-Nb_3Cl_8 phase. These investigations are continuing.

Conclusions

We have reported here the first characterized unsolvated intercalation product from a binary metal halide with a very electropositive alkali metal. It is surprising to find this reaction with an early-transition-metal compound. It was shown that $NaNb_3Cl_8$ could form either a β- or β'-structure in order to reduce edge-bridging (X2) M–L π interactions and provide for directed lone pair to cation interactions in the B-gap. So as to reduce terminal (X1) M–L orbital interactions and likewise give directed lone pair to cation interactions in the A-gap, the β'-structure is formed. Thus, a structural transition ensues whereby all Nb_3Cl_8 cluster layers must shift relative to one another at all van der Waals gaps, and this enhances ion diffusion. These results, discussed in connection with results for other $M_3X_8^{n-}$ cluster derivatives, seem to indicate that M–L antibonding orbital interactions have a strong influence on M–M bond distances within the cluster triangles. The α-phase is the stable form for Nb_3Cl_8 because other related forms cause much too close contacts between directional long-pair orbitals of the edge-bridging (X2) atoms.

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[21] Cotton, F. A.; Diebold, M. P.; Roth, W. J. *J. Am. Chem. Soc.* **1987**, *109*, 2833.

[22] Cotton, F. A.; Kibala, P. A.; Roth, W. J. *J. Am. Chem. Soc.* **1988**, *110*, 298.

[23] Sägebarth, M. Dissertation, Universität Stuttgart, 1989.

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The Possible Existence of a Heteronuclear Octahedral Hypercloso Cluster: Can N_2 or an Alkyne Be Complexed through a M_4L_n Square?

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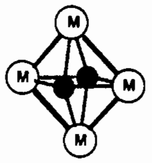
In previous theoretical studies, we have rationalized the electronic structure of a class of octahedral organometallic clusters of general formula $L_nM_4E_2$, shown in **1**, where M is a transition



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metal and E (black dot in **1**) is a main-group atom or a conical fragment from the third and fourth period, such as S, Se, PR, GeR, ...[1] The total valence electron count adopted by these closo clusters is either 66 electrons, i.e. seven skeletal electron pairs (SEP's) or 68 electrons (eight SEP's). The 66-electron count satisfies the polyhedral skeletal electron pair theory (PSEP),[2] while the 68-electron count corresponds to the occupation of an extra skeletal MO, which is weakly π-antibonding between the metal atoms.[1] In these clusters, because of the difference in the covalent radii of M and E, and consequently because of the difference in M–M and M–E bond lengths, the two E atoms capping the metallic square are forced to be rather close to each other (the E···E distance is about 20% longer than the one expected for a single bond). We have shown that such a short E···E contact can exist only because the corresponding electronic interaction is significantly bonding, whatever is the cluster electron count (seven or eight SEP's).

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[1] (a) Halet, J.-F.; Hoffmann, R.; Saillard, J.-Y. *Inorg. Chem.* **1985**, *24*, 1695. (b) Halet, J.-F.; Saillard, J.-Y. *New J. Chem.* **1987**, *11*, 315. (c) Albright, T. A.; Yee, K. A.; Saillard, J.-Y.; Kahlal, S.; Halet, J.-F.; Leigh, J. S.; Whitmire, K. H. *Inorg. Chem.* **1991**, *30*, 1179.

[2] (a) Wade, K. *J. Chem. Soc., Chem. Commun.* **1971**, 792. (b) Mingos, D. M. P. *Nature (London) Phys. Sci.* **1972**, *236*, 99. (c) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1. (d) Wade, K. In *Transition Metal Clusters*; Johnson, B. F. G., Ed.; Wiley and Sons: New York, 1980, p 193. (e) Mingos, D. M. P. *Acc. Chem. Res.* **1984**, *17*, 311.

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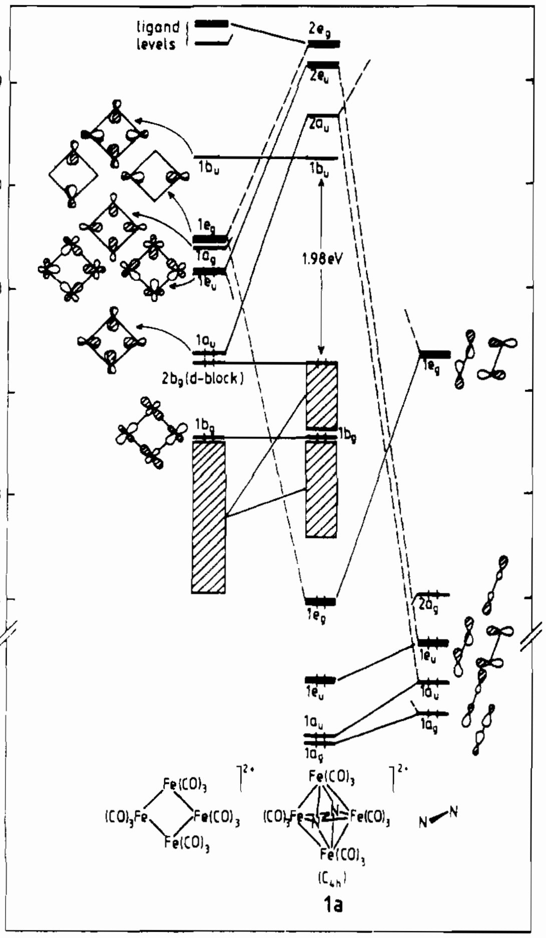

Figure 1. MO interaction diagram of the model complex [$Fe_4(CO)_{12}$-(μ_4-N)]$^{2+}$ (**1a**).

These results prompted us to explore, using extended Hückel (EH) calculations, the possibility of existence of a cluster of type **1** in which E belongs to the second period, such as BR, CR, NR, or N. Indeed, in this case, the size effect mentioned above is very important. For example, in a cluster of formula $Fe_4(CO)_{12}(\mu_4\text{-}N)_2$, assuming standard Fe–Fe (2.50 Å) and Fe–N (1.90 Å) bond distances, the N–N separation is short (1.39 Å) and comparable to a single N–N bond (1.40 Å). Thus we prefer the formulation $Fe_4(CO)_{12}(\mu_4\text{-}N_2)$.

The coordination of dinitrogen in mononuclear transition-metal complexes has stimulated several theoretical ab initio analyses.[3] This kind of calculation cannot obviously be used for larger molecules. We must mention that EH calculations on dinitrogen complexes are in good qualitative accordance with the available ab initio studies. This has been checked by comparing EH and ab initio[3] results on the complex $Rh(Cl)(PH_3)_2(N_2)$.

The MO diagram of the hypothetical cluster $Fe_4(CO)_{12}(\mu_4\text{-}N_2)^{2+}$ (**1a**), shown in Figure 1, is obtained from the interaction of the metallic square $Fe_4(CO)_{12}$ fragment with the dinitrogen moiety. Obviously such a structure is strongly favored for a 64-electron count (six SEP's): a large HOMO–LUMO gap (1.98 eV), separating the occupied bonding and nonbonding MO's from the antibonding ones, is then obtained. Therefore, we suggest that hypercloso clusters of type **1**, such as $[Fe_4(CO)_{12}(\mu_4\text{-}N_2)]^{2+}$ or $Fe_4(CO)_{11}(\mu_4\text{-}N_2)$ might exist. The two-electron deficiency with respect to the PSEP theory originates from the metallic 1a$_u$ frontier orbital, which is strongly destabilized after interaction with the N_2 entity and thus cannot be occupied (2a$_u$ MO in **1a**). This metallic a$_u$ MO is stabilized somewhat and occupied in the 66-electron $Fe_4(CO)_{12}(\mu_4\text{-}P)_2$ analogue model complex **1b**.[1] The 2a$_u$ MO in **1a** is, to a first approximation the "nonbonding" component resulting from the interaction of the metallic a$_u$ FMO with the two N_2 orbitals of same symmetry (the low-lying lone pair 1a$_u$ combination and the very high-lying σ^*_{N-N} 2a$_u$ orbital, which is not shown in Figure 1). The magnitude of interaction between two nondegenerate orbitals *i* and *j* is proportional to $S_{ij}^2/(E_i - E_j)$. In **1a**, for both energy and overlap reasons, the major interaction for this three-orbital pattern occurs between the metallic FMO and one of the low-lying nitrogen lone pair combinations (1a$_u$). The strong $\langle 1a_u\ (Fe_4)|\ 1a_u\ (N_2)\rangle$ overlap is due to the proximity of the N atoms to the metallic square. The 1a$_u$ N_2 lone pair combination is stabilized and the metallic 1a$_u$ FMO highly destablized. The interaction of the latter with the very high-lying 2a$_u$ σ^*_{N-N}, nearly 14 times less important than the previous one, is not sufficient to prevent it to be strongly pushed up in energy. The resulting 2a$_u$ MO, although mainly metallic in character, possesses a rather important N_2 contribution (16%) as shown in Figure 2a. Moreover, the metallic participation (20%) in the bonding combination (1a$_u$ MO in **1a**) indicates that the N_2 1a$_u$ lone pair orbital is strongly involved in the cluster core bonding (see Figure 2b). The other N_2 lone pair combination of symmetry 2a$_g$ interacts very poorly with vacant orbitals of the metallic core. Its electron occupation after interaction is 1.98, while it is 1.60 for the 1a$_u$ component.

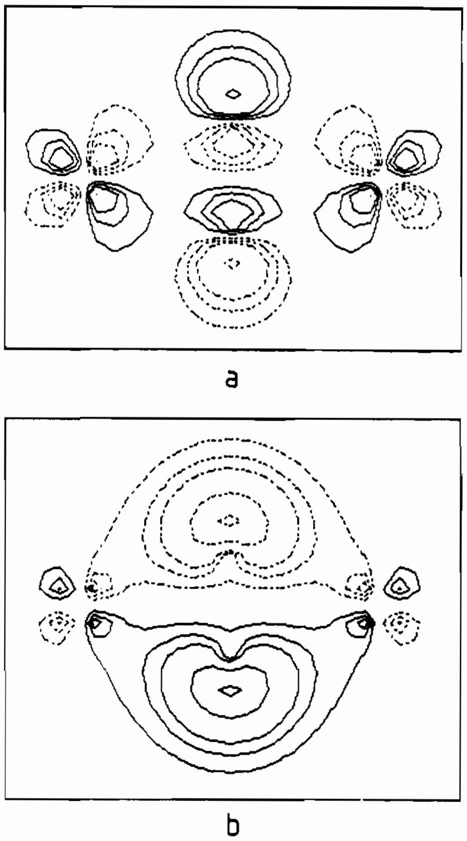

Figure 2. (a) Contour map of the unoccupied 2a$_u$ MO of **1a** plotted in a Fe_2N_2 plane. (b) Contour map of the occupied 1a$_u$ MO of **1a** plotted in a Fe_2N_2 plane.

The situation is rather different in the 66-electron model **1b** since this time the interaction of the metallic 1a$_u$ FMO with the low-lying a$_u$ P_2 lone pair combination is only half of the one with the high-lying σ^*_{P-P} orbital. Therefore, the metallic FMO is slightly stabilized after interaction and occupied. The comparison of the computed overlap populations in **1a** and **1b** indicates that the loss of two electrons might weaken the Fe–Fe bonds since the Fe–Fe overlap populations drop from ca. 20% (0.107 vs 0.140 respectively). The computed Fe–N overlap populations, 0.298, are in the order of magnitude of the values usually obtained for similar bonds in heteronuclear organometallic clusters.

Important forward donation (1.58 electrons) from occupied N_2 orbitals into acceptor metallic FMO's and back-donation (2.25 electrons) from metallic orbitals toward N_2 vacant orbitals nec-

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(3) Sakaki, S.; Morokuma, K.; Ohkubo, K. *J. Am. Chem. Soc.* **1985**, *107*, 2686 and references therein.

essarily lead to a weakening of the N–N bond order. The N–N overlap population decreases from 1.19 in free N_2 (of identical internuclear separation) to 0.72 for the complexed N_2. Despite the rather important overlap population diminution, the N–N interaction is still strongly bonding. After interaction, the σ_{N-N}, π_{N-N}, and π^*_{N-N} orbitals are formally occupied while the σ^*_{N-N} orbital ($2a_u$) is vacant. Consequently, we conclude that there is an intracluster nitrogen–nitrogen bond in **1a** explaining the two electron deficiency.

When the N_2 ligand is replaced by acetylene (keeping the same bond distances) the HOMO–LUMO gap corresponding to the 64-electron count is somewhat reduced (0.98 eV), because of the weaker M–E antibonding character of the a_u MO, which becomes the LUMO in the acetylene case. Therefore, the existence of an hypercloso cluster of structure **1** having E = CR appears still possible, but such a cluster should be less stable than its N_2 homologue. Indeed, the presence of lone pairs on the E_2 ligand appears to be a stabilizing factor for such a molecule. Calculations in which the N–N and C–C separations vary from 1.15 to 1.50 Å lead to similar qualitative results.

It is generally admitted that dinitrogen, a better σ-donor than a π-donor, prefers to be coordinated in an end-on fashion rather than a side-on fashion. It is interesting to note that in **1a**, where N_2 is side-on complexed, *both* types of orbitals (σ lone pairs and π-bonding) are involved in the donation process to the metallic square.

Related and Known Structures

Intracluster main-group–main-group-bonding interactions have already been noticed in organometallic clusters. Five-vertex compounds $[W(CO)_5]_3(\mu_3\text{-}E_2)$ exhibit no metal–metal interactions but strong E–E bonding interactions. The E–E bond order is considered to be larger than 1.[4] A very short C–C contact of 1.275 Å is observed for the dicarbido unit complexed through a highly distorted metallic rectangle in the 70-electron compound $Ru_4(CO)_{12}(\mu\text{-}PPh_2)_2(\mu_4\text{-}C_2)$.[5]

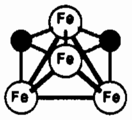
Intracluster N-N bond observed in our hypothetical hypercloso complex **1a** is reminiscent of the situation encountered in the electron deficient $CpME_nMCp$ triple-decker complexes where a metal–metal bond is present through the inorganic E_n ring.[6] As in **1a**, electron deficiency in these hypercloso triple-decker species is attributed to the intracluster bond.

Note finally that with only one nitrogen atom, i.e., a *nido*-Fe_4N square pyramid, the situation is analogous to the one encountered for the Fe_4P_2 model **1b**. Rather large HOMO/LUMO gaps for the expected electron counts of seven and eight SEP's are computed (0.87 and 1.01 eV respectively).[1a,7]

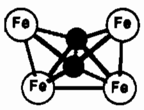
Skeletal Isomers

The PSEP theory[2] predicts alternative structures for 64-electron M_4E_2 clusters, based on the bicapped tetrahedron geometry, as shown in **2**. Our calculations indicate that, in fact, **2a** is unstable for any electron count.[8] A large HOMO/LUMO gap of 1.54 eV is calculated for **2b** with an electron count of 68, i.e. 4 electrons more than predicted by PSEP rules.[9] The **2c** model satisfies the PSEP rules since a HOMO/LUMO gap of 1.79 eV is observed with the favored 64-electron count. However, for this electron count, **2c**, which can be derived from **1a** by opening one metal–metal bond (a symmetry allowed process), is found unstable with respect to **1a**. Thus **1a** appears to be the only possible skeletal arrangement for a 64-electron six-vertex M_4N_2 organometallic cluster.

2a



2b



2c

Let us remark that cluster **1a** can be described from the condensation of a 40-electron M_2E_2 tetrahedron with a 24-electron M_2 organometallic fragment.[10] It is also structurally (and in some ways electronically) related to the 70-electron $[Co_4(CO)_{11}E_2]^{2-}$ (E = Bi, Sb) anions that adopt structure **2c**.[1c,11,12]

Finally, note that this type of hypothetical hypercloso cluster can be considered as an extention of the series of the compounds consisting of a μ_4-alkyne, -nitrile, or -azoalkane ligand coordinated to M_4 frameworks recently described and analyzed by Vahrenkamp et al.[13]

Computational Procedure

The calculations have been made within the extended Hückel formalism,[14] using the weighted H_{ij} formula.[15] The following bond distances (Å) have been used (see also text): Fe–C(O) = 1.85; C–O = 1.15; C–H = 1.09. The atomic parameters were taken from the literature.[1]

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(4) See: (a) Sigwarth, B.; Zsolnai, L.; Berke, H.; Huttner, G. *J. Organomet. Chem.* **1982**, *226*, C5. (b) Huttner, G.; Weber, U.; Sigwarth, B.; Scheidsteger, O. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 215. (c) Huttner, G.; Weber, U.; Zsolnai, L. *Z. Naturforsch.* **1982**, *376*, 707.

(5) Bruce, M. I.; Snow, M. R.; Tiekink, E. R. T.; Williams, M. L. *J. Chem. Soc., Chem. Commun.* **1986**, 701.

(6) Tremel, W.; Hoffmann, R.; Kertesz, M. *J. Am. Chem. Soc.* **1989**, *111*, 2030 and references therein.

(7) Halet, J.-F.; Saillard, J.-Y.; Lissillour, R.; McGlinchey, M. J.; Jaouen, G. *Organometallics* **1986**, *5*, 135.

(8) Such a E_2 coordination is observed in the 68-electron compound $Fe_2Ni_2(C_5H_5)_2(CO)_6(\mu_4\text{-}C_2Ph_2)$, whose metal atoms describe an almost flat distorted square: Sappa, E.; Manotti Lanfredi, A. M.; Predieri, G.; Tiripicchio, A.; Carty, A. J. *J. Organomet. Chem.* **1985**, *288*, 365.

(9) Though N and CH fragments are isolobal, their interaction with a tetrahedral $Fe_4(CO)_{12}$ unit leads to different MO diagrams. This difference is mainly due to their different electronegativity. Indeed, a HOMO/LUMO gap of 0.96 eV is computed for the expected electron count of 64 in $[Fe_4(CO)_{12}(\mu_3\text{-}CH)_2]^{2+}$ in agreement with the reported structure of $WOs_3(C_5H_5)(CO)_9(\mu_3\text{-}CTol)_2$: Park, J. T.; Shapley, J. R.; Churchill, M. R.; Bueno, C. *J. Am. Chem. Soc.* **1983**, *105*, 6182.

(10) (a) Hoffman, D. M.; Hoffmann, R.; Fisel, C. R. *J. Am. Chem. Soc.* **1982**, *104*, 3858. (b) Goldberg, K. I.; Hoffman, D. M.; Hoffmann, R. *Inorg. Chem.* **1982**, *21*, 3863.

(11) Martinengo, S.; Ciani, G. *J. Chem. Soc., Chem. Commun.* **1987**, 1589.

(12) Leigh, J. S.; Whitmire, K. H.; Yee, K. Y.; Albright, T. A. *J. Am. Chem. Soc.* **1989**, *111*, 2726,

(13) (a) Bantel, H.; Hansert, B.; Powell, A. K.; Tasi, M.; Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1059. (b) For a theoretical study see: Kahlal, S.; Halet, J.-F.; Saillard, J.-Y. *New J. Chem.*, in press.

(14) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397.

(15) Ammeter, J. H.; Bürgi, H.-B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686.

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Hydride Locations and Bonding Studies in Some Silyl Polyhydride Rhenium Complexes

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Recently, Crabtree and his co-workers synthesized and characterized several rhenium polyhydride complexes.[1,2] Although the positions of the heavy atoms in these rhenium complexes were determined by X-ray crystallography, the positions of the H atoms are unknown. Crabtree and his co-workers based suggested structure for these complexes on NMR spectroscopy. For example, a pentagonal-bipyramidal structure was proposed for the 7-coordinate complex $ReH_2(EPh_3)(CO)(PMe_2Ph)_3$ (E = Si, Sn), where the two H atoms are located in the equatorial plane. For $ReH_6(SiR_3)(PPh_3)_2$, a classical 9-coordinate tricapped trigonal-prismatic structure was proposed with the two PPh_3 ligands and the silyl group occupying the three equatorial sites, i.e. the

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(1) Luo, X.-L.; Schulte, G. K.; Demou, P.; Crabtree, R. H. *Inorg. Chem.* **1990**, *29*, 4268.

(2) Luo, X.-L.; Baudry, D.; Boydell, P.; Nierlich, M.; Ephritikhine, M.; Crabtree, R. H. *Inorg. Chem.* **1990**, *29*, 1511.

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