analysis, if we take the H(1) hyperfine tensor estimated for a single interacting proton from ENDOR and EPR line-narrowing and assign signs such that $A^{H}(1) = [+15, -22, -25]$ then $a_{iso} \approx -11$ MHz; the resulting dipolar tensor also appears to be acceptable[16] for the expected Ni–H distance,[25] $d \gtrsim 1.5$ Å. Although we tend to favor this assignment, these data also appear to be consistent with a not previously considered assignment of H(1) to an X–H (X = O, S, or N) moiety where the proton is involved in a direct (agostic) interaction with nickel.[26] Such an interaction is thought to stabilize higher valence states and again is most appropriate for Ni(III). Changing the proposed signs of the hyperfine tensor would give $a_{iso} \approx +11$ MHz, as expected for direct interaction; the dipolar interaction calculated from this or other assignments is reasonable for the expected Ni–H distance of $d \geq 2$ Å. It is straightforward to construct catalytic cycles that involve an intermediate with such a structure. Finally, we note the possibility of direct interaction with H_2. In this case, $d > 1.5$ Å is expected,[27] and formulation as a lower value state, Ni(I), would be most appropriate.

Conclusions

Our present EPR and ENDOR studies permit the following conclusions about the nickel site of *D. gigas* hydrogenase.

(1) The Ni-A site is inaccessible to solvent protons, consistent with the suggestion reached by activity studies that the enzyme in the Ni-A state is inactive.

(2) The Ni-C site is accessible to protons from solvent and/or gaseous hydrogen. This is in agreement with recent electron spin echo measurement[8] and is consistent with the Ni-C site having a catalytic role in H_2 activation. The ENDOR measurements have now characterized the exchangeable hydrogenic species. The Ni-C center exhibits one type of exchangeable proton that has a large hyperfine coupling ($A^{H}(1) = 16.8$ MHz). Analysis rules out as assignment an H_2O (or OH^-) or as a hydride bound axially to the Ni-C. Three other modes of direct interaction between H(1) and Ni appear to be possible: as an in-plane hydride, as an X–H proton directly interacting with nickel (agostic interaction), and even as H_2. A second type of exchangeable proton is associated with the Ni-C and has a smaller hyperfine coupling ($A^{H}(2) \approx 4.4$ MHz), which is consistent with the proton being associate with H_2O (or OH^-) bound to the Ni-C.

(3) At least one type of exchangeable deuteron associated with the Ni-C center remains associated with the Ni-B center after oxidation of the Ni-C. The small coupling is consistent with that of H_2O (or OH^-) bound to the Ni-B.

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Registry No. H_2, 1333-74-0; Ni, 7440-02-0; hydrogenase, 9027-05-8.

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(23) Werst, M. M.; Kennedy M.-C.; Beinert, H.; Hoffman, B. M. *Biochemistry*. In press.

(24) Box, H. C.; Budzinski, E. E.; Lilga, K. T.; Freund, H. G. *J. Chem. Phys.* **1970**, *53* (*3*), 1059–1065.

(25) Teller, R. G.; Bau, R. *Struct. Bonding* (*Berlin*) **1981**, *41*, 1–82.

(26) Brookhart, M.; Green, M. L. H.; Wong, L.-L. *Prog. Inorg. Chem.* **1988**, *36*, 1–124.

(27) (a) Kular, G. J. *Au. Chem. Res.* **1988**, *21*, 120. (b) Ricci, J. S.; Koetzle, T. F.; Bautista, M. T.; Hoptede, T. M.; Morris, R. H.; Sawyer, J. F. *J. Am. Chem. Soc.* **1989**, *111*, 8823–8827.

Correlation of Nuclear Magnetic Deshielding with Compression of Interstitial Atoms in Transition-Metal Clusters

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Abstract: A correlation of NMR shift with compression is demonstrated for interstitial carbide and nitride in transition-metal clusters, from the trigonal prism to the octahedron, square prism and butterfly geometries. The nuclear magnetic shielding decreases with a decrease in the cavity radius, more clearly in simple clusters than in more complicated ones with capping or bridging species. This correlation explains the unusual shift pattern observed for interstitial carbides and nitrides. All cluster carbides are compressed below the normal covalent radius of carbon, and the shieldings are very low, below the normal range (except for carbonium ions). Interstitial nitride is less compressed (or even expanded from its normal radius), and nitride shieldings are much higher, lying within the range observed for organic compounds. This periodicity can be shown to extend to other interstitials, and the correlation is observed in non-metal cages also. Comparable correlations and the factors in nuclear magnetic shielding that are affected by the compression are discussed.

To the many correlations of NMR shift with molecular strain,[1] we now add a correlation with compression for interstitial carbide and nitride in transition-metal clusters. The figures and tables (which give references for individual clusters) show that nuclear shielding decreases with decrease in the cavity radius ($r(\mathrm{I}) = r(\mathrm{MI})_{av} - r(\mathrm{MM})_{av}/2$, where the metal M is bonded to the interstitial I). In each figure, the shielding decreases from the trigonal prism to the octahedron-based species, including the square prism and butterfly (in which the interstitial shares all its valence electrons in σ and π bonding with the cluster[2,3]). Outliers are clusters with distorted cavities and (or) capping or bridging species; differences between (fluxional) solution and solid-state

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(1) Mason, J., Ed. *Multinuclear NMR*; Plenum: New York, 1987.

(2) Bradley, J. S. *Adv. Organomet. Chem.* **1983**, *22*, 1 and references therein.

(3) Gladfelter, W. L. *Adv. Organomet. Chem.* **1985**, *24*, 41 and references therein.

Table I. NMR Shifts and Atomic Radii for Interstitial Carbide in Metal Clusters

compound	$\delta(^{13}C)$/ ppm	core geometry[a]	r(C)/ pm	ref
$[Rh_6(\mu_6\text{-}C)(CO)_{15}]^{2-}$	264.7	tp	73.5	*b*
$[\{Rh_6(\mu_6\text{-}C)(CO)_{15}\}_2(\mu_6\text{-}Ag)]^{3-}$	272.7	dist tp	74.0	*c*
$[Rh_6(\mu_6\text{-}C)(CO)_{15}(\mu_3\text{-}CuNCMe)_2]^{2-}$	300.3	tp	73.7	*c*
$[Co_6(\mu_6\text{-}C)(CO)_{15}]^{2-}$	330.5	tp	67.2	*d*
$[Co_8(\mu_8\text{-}C)(CO)_{18}]^{2-}$	387.9	dist sa	[73]	*d*
$[Os_{10}(\mu_6\text{-}C)(CO)_{24}(\mu_4\text{-}H)]^-$	409	oct	60.0	*e*
$[Re_7(\mu_6\text{-}C)(CO)_{21}]^{3-}$	423.6	dist oct	62.5	*f*
$[Re_8(\mu_6\text{-}C)(CO)_{24}]^{2-}$	431.3	dist oct	62.0	*g*
$[Rh_6(\mu_6\text{-}C)(CO)_{13}(\mu_3\text{-}AuPPh_3)_2]$	452.5	dist oct	61.6	*h*
$[Ru_{10}(\mu_6\text{-}C)_2(CO)_{24}]^{2-}$, −60 °C	457	dist oct	64.0	*i*
$[Ru_6(\mu_6\text{-}C)(CO)_{16}\{Cu(NCMe)\}_2]$	458	dist oct	60.0	*j*
$[Ru(\mu_6\text{-}C)(CO)_{16}]^{2-}$	458.9	oct	61.3	*k*
$[Rh_6(\mu_6\text{-}C)(CO)_{13}(\mu_2\text{-}H)]^-$	460.4	dist oct	59.5	*l*
$[RhFe_3(\mu_4\text{-}C)(CO)_{12}]^-$	461.1	bu	59.6	*m*
$[(\mu_2\text{-}H)Fe_4(\mu_4\text{-}C)(CO)_{12}]^-$	464.2	bu	58.0	*n*
$[Fe_4(\mu_4\text{-}C)(CO)_{13}]$	468.9	bu	58.4	o
$[Rh_6(\mu_6\text{-}C)(CO)_{13}]^{2-}$	470.0	dist oct	59.3	*l*
$[CoFe_4(\mu_5\text{-}C)(CO)_{14}]^-$	476.9	sp	57.6	*m*
$[Fe_4(\mu_4\text{-}C)(CO)_{12}]^{2-}$	478.0	bu	57.2	*p*
$[Fe_6(\mu_6\text{-}C)(CO)_{16}]^{2-}$	484.6	oct	55.5	*p*
$[Fe_5(\mu_5\text{-}C)(CO)_{15}]$	486.0	sp	57.9	*p*

[a] Key: dist, distorted; tp, trigonal prism; sa, square antiprism; oct, octahedron; bu, butterfly; sp, square pyramid. [b] Albano, V. G.; Chini, P.; Martinengo, S.; McCaffrey, D. J. A.; Strumolo, D.; Heaton, B. T. *J. Am. Chem. Soc.* **1974**, *96*, 8106. [c] Heaton, B. T.; Strona, L.; Martinengo, S.; Strumolo, D.; Albano, V. G.; Braga, D. *J. Chem. Soc., Dalton Trans.* **1983**, 2175. [d] Albano, V. G.; Chini, P.; Ciani, G.; Sansoni, M.; Strumolo, D.; Heaton, B. T.; Martinengo, S. *J. Am. Chem. Soc.* **1976**, *98*, 5027; Martinengo, S.; Strumolo, D.; Chini, P.; Albano, V. G.; Braga, D. *J. Chem. Soc., Dalton Trans.* **1985**, 35; Chini, P. *Adv. Organomet. Chem.* **1980**, *200*, 37. [e] Constable, E. C.; Johnson, B. F. G.; Lewis, J.; Pain, G. N.; Taylor, M. J. *J. Chem. Soc., Chem. Commun.* **1982**, 754. [f] Ciani, G.; D'Alfonso, G.; Freni, M.; Romiti, P.; Sironi, A. *J. Chem. Soc., Chem. Commun.* **1982**, 339. [g] Ciani, G.; D'Alfonso, G.; Freni, M.; Romiti, P.; Sironi, A. *J. Chem. Soc., Chem. Commun.* **1982**, 705. [h] Fumagalli, A.; Martinengo, S.; Albano, V. G.; Braga, D.; Grepioni, F. *J. Chem. Soc., Dalton Trans.* **1989**, 2343. [i] Hayward, C.-M. T.; Shapley, J. R.; Churchill, M. R.; Bueno, C.; Rheingold, A. L. *J. Am. Chem. Soc.* **1982**, *104*, 7347. [j] Bradley, J. S.; Pruett, R. L.; Hill, E.; Ansell, G. B.; Leonowicz, M. E.; Modrick, M. A. *Organometallics* **1982**, *1*, 748. [k] Bradley, J. S. *Adv. Organomet. Chem.* **1983**, *22*, 1. Correction of the $\delta(^{13}C)$ value given by: Bradley, J. S.; Ansell, G. B.; Hill, E. W. *J. Organomet. Chem.* **1980**, *184*, C33. [l] Bordoni, S.; Heaton, B. T.; Seregni, C.; Strona, L.; Hursthouse, M. B.; Thornton-Pett, M.; Martinengo, S. *J. Chem. Soc., Dalton Trans.* **1988**, 2103. Correction of $\delta(^{13}C)$ for $[Rh_6C(CO)_{13}]^{2-}$ given by: Heaton, B. T.; Strona, L.; Martinengo, S. *J. Organomet. Chem.* **1981**, *215*, 415. [m] Hriljac, J. A.; Swepston, P. N.; Shriver, D. F. *Organometallics* **1985**, *4*, 158. [n] Holt, E. M.; Whitmire, K. H.; Shriver, D. F. *J. Organomet. Chem.* **1981**, *213*, 125. [o] Bradley, J. S.; Ansell, G. B.; Leonowicz, M. E.; Hill, E. W. *J. Am. Chem. Soc.* **1981**, *103*, 4968. [p] Bradley, J. S. *Philos. Trans. R. Soc. London* **1982**, *308*, 103.

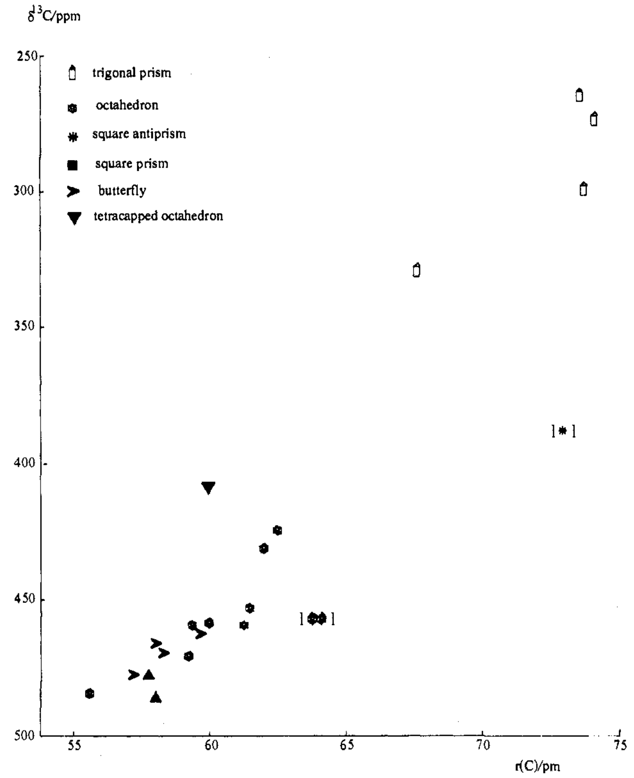

Figure 1. Correlation of carbide shifts with atomic radius in metal clusters.

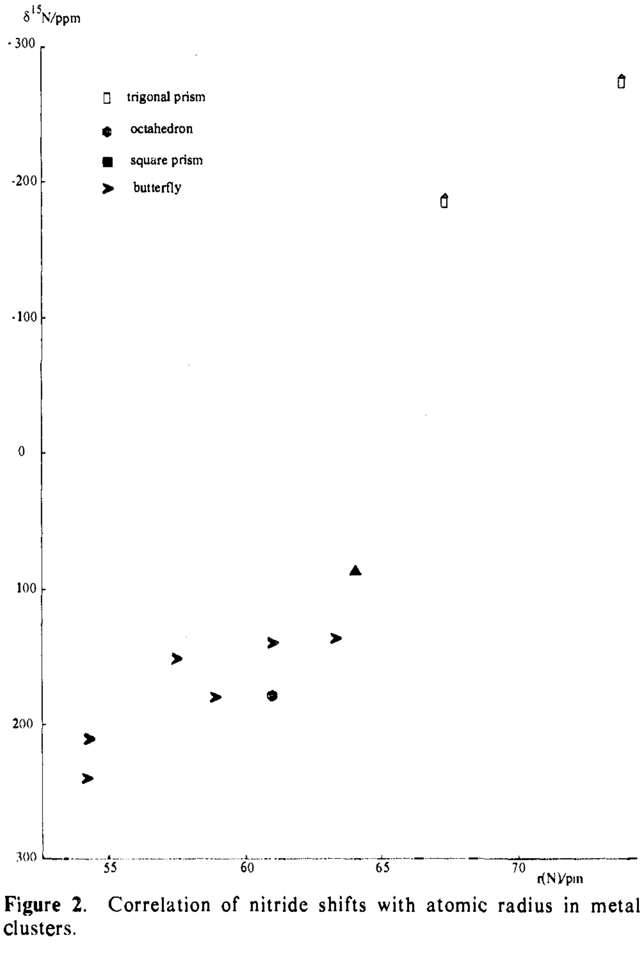

Figure 2. Correlation of nitride shifts with atomic radius in metal clusters.

species also increase the scatter.

This correlation explains the anomalous pattern[4] that emerged with the first clusters observed to contain interstitial nitrogen, the rhodium and cobalt trigonal prisms,[5] and their carbide analogues. Interstitial carbides are strongly deshielded, appearing below the normal region for organic compounds (except for carbonium ions[6]), but the shielding of corresponding (isostructural, isoelectronic) nitrides is much higher, within the usual range for organic compounds (Tables I and II). Normally, similar shift patterns are observed for neighbors in the periodic table. For carbon and nitrogen,[7] high shielding is observed in singly bonded compounds (alkanes, NH_4^+, amines), decreasing in linear groups ($CH{\equiv}CH$, N_2), then aromatics, and then doubly bonded compounds (Figures 1 and 2). The nitrogen range is extended by groups (diazenes,

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(4) See: Reference 1, p 357. There was an apparent symmetry-related anomaly, which disappeared with the correction of early reports of (higher) shielding for two octahedral carbides (noted in the references to Table I).

(5) Martinengo, S.; Ciani, G.; Sironi, A.; Heaton, B. T.; Mason, J. *J. Am. Chem. Soc.* **1979**, *101*, 7095.

(6) Olah, G. A; White, A. M. *J. Am. Chem. Soc.* **1969**, *91*, 5801.

(7) See: Reference 1, Chapter 12. Mason, J. *Chem. Rev.* **1981**, *81*, 205. Numerically, the shifts are scaled approximately in proportion to the radial factor $\langle r^{-3}\rangle_{2p}$ on which the paramagnetic circulation depends, where r_{2p} is the 2p-electron radius. This factor is approximately half as large for carbon as for the (more electronegative) nitrogen, so the shift scale in Figure 1 is twice that of Figure 2 for comparability. Note that whereas the carbon reference TMS has a shift near that of CH_4, the nitrogen reference nitromethane is deshielded by 360 ppm relative to NH_4^+.

Table II. Nitrogen Shifts and Atomic Radii for Interstitial Nitride in Metal Clusters

compound	$\delta(^{15}N)^a$/ ppm	core geometry^b	r(N)/ pm	ref
$[Rh_6(\mu_6\text{-}N)(CO)_{15}]^-$	−273	tp	73.9	*c*
$[Co_6(\mu_6\text{-}N)(CO)_{15}]^-$	−184	tp	67.2	*c*
$[Ru_5(\mu_5\text{-}N)(CO)_{14}]^-$	85.3	sp	64.0	*d, e*
$[FeRu_3(\mu_4\text{-}N)(CO)_{10}\{P(OMe)_3\}_2]^-$	134.4	bu	63.3	*f*
$[FeRu_3(\mu_4\text{-}N)(CO)_{12}]^-$	140.5	bu, Fe_{hinge}	61	*g*
$[FeRu_3(\mu_4\text{-}N)(CO)_{12}(\mu_2\text{-}AuPPh_3)]$	153.4	bu, Fe_{wing}	57.5	*h*
$[FeRu_3(\mu_4\text{-}N)(CO)_{12}]^-$	179.6	bu, Fe_{wing}	59	*g*
$[Ru_6(\mu_6\text{-}N)(CO)_{16}]^-$	180.2	oct	61^i	*d, e*
$[Fe_4(\mu_4\text{-}N)(CO)_{12}(\mu_2\text{-}H)]$	211	bu	54.3	*d, j*
$[Fe_4(\mu_4\text{-}N)(CO)_{12}]^-$	238.7	bu	54.2	*d, k*

[a] Relative to neat liquid nitromethane. [b] See notes to Table I. μ_2-H and μ_2-AuPPH$_3$ bridge the MM hinge. [c] Martinengo, S.; Ciani, G.; Sironi, A.; Heaton, B. T.; Mason, J. *J. Am. Chem. Soc.* **1979**, *101*, 7095. [d] Gladfelter, W. L. *Adv. Organomet. Chem.* **1985**, *24*, 41. [e] Blohm, M. L.; Gladfelter, W. L. *Organometallics* **1985**, *4*, 45. [f] The phosphite groups occupy wing positions. Blohm, M. L.; Fjare, D. E.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1986**, *108*, 2301. [g] The radii are estimated (by comparison with other Fe, Ru butterfly structures) from the averaged values observed for the disordered structure. Fjare, D. E.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1984**, *106*, 4799. [h] Blohm, M. L.; Gladfelter, W. L. *Inorg. Chem.* **1987**, *26*, 459. [i] This structure has not been reported, but the cavity radius is expected to resemble that of the isostructural carbide. [j] Tachikawa, M.; Stein, J.; Muetterties, E. L.; Teller, R. G.; Beno, M. A.; Gebert, E.; Williams, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 6648. [k] Blohm, M. L.; Fjare, D. E.; Gladfelter, W. L. *Inorg. Chem.* **1983**, *22*, 1004.

nitrosyls) with low-energy paramagnetic (deshielding) circulations of lone-pair electrons ($n(N) \rightarrow \pi^*$), which are not present in the clusters. But the nitride shifts in trigonal prisms are comparable to those in amines, and those in octahedron-based clusters are comparable to those in diazenes.

The strong deshielding of the interstitial carbides can now be "explained" by the compression. All have significantly less than the carbon covalent radius (77 pm) in contrast to interstitial nitrogen. On the other hand, nitride in the Rh_6 prism is expanded relative to the covalent radius of 70 pm for tetrahedral nitrogen, and metal cluster cores are contracted in nitrides relative to carbides.[3] Boride, oxide, and phosphide interstitials confirm this periodicity: the oxides are even more highly shielded (compared with the normal range of shieldings for this nucleus) than the nitrides, and interstitial borides and phosphides are strongly deshielded.[8]

The correlation extends to non-metal cages and to anisotropies in the shielding of the interstitial nucleus: thus, the shielding of ^{129}Xe trapped in β-quinol, β-phenol, or hydrate clathrates, or in a hydrogen mordenite, decreases with decrease in the free diameter of the cavity. Moreover, in an elongated cage the ^{129}Xe shows higher shielding along the axis of elongation, and in a flattened (oblate spheroidal) cage there is higher shielding along the axis.[9] Ab initio calculations on two aromatic cages, the C_{60} *t*-icosahedron and the $C_{20}{}^+$ dodecahedron, show lower shielding for a test magnetic dipole at the center of the smaller cluster compared with the larger cluster.[10]

Counterexamples to "compression–deshielding" are *in*creases in cobalt[11,12] shielding with pressure in d^6 complexes and "normal" isotope[13] and temperature[12] shifts. Replacement of a substituent by a heavier isotope usually increases nuclear shielding, because of rovibrational shortening of the bond, as the heavier isotopomer sits lower in the potential well; temperature shifts have a similar rationale.[13] But *de*shielding with bond shortening is observed for group I–III metal hydrides in $^{2/1}H$ isotope shifts[14,15] and for Cd and Hg in $M(^{13/12}CH_3)_2$ isotope shifts.[16] Ab initio calculations show that increased Li^+H^- polarization on bond extension decreases the major ($\sigma \rightarrow \pi^*$) paramagnetic circulation, increasing the Li shielding, whereas in HF, which has a "normal" sign of isotope shift, increased H^-F^+ polarization of the antibonding σ^* orbital with bond extension enhances the major ($\pi^* \rightarrow \sigma^*$) paramagnetic circulation, deshielding fluorine.[14] Pressure and temperature shifts for d^6 transition metals are "normal" in sign, being dominated by the decrease in (d–d) excitation energy on bond extension.[12]

For interstitial carbide or nitride the ($\sigma \rightarrow \sigma^*$) paramagnetic circulation decreases with decrease in the radial factor $\langle r^{-3}\rangle_{2p}$, which decreases with increase in negative charge (a nephelauxetic effect).[1] Fenske–Hall and EHMO calculations[17] show that interstitial carbide carries a negative charge of around −0.5 e, becoming more negative with increase in hole size. This supports increased shielding in a larger cavity, and also from carbon to nitrogen (which retains more electronic charge), as does destabilization of the 2p orbitals from nitride to carbide, and with compression.[18] The calculation of these and other factors of importance (such as the imbalance of charge in the p orbitals, the contribution of $\sigma \leftrightarrow \pi$ circulations in the square prisms and butterflies, and diamagnetic contributions) is in hand.

We hope this correlation will prompt further examples and counterexamples of compression and deshielding. We are finding shift changes in the solid state with compression in crystal packing.[19]

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(8) Mason, J. Manuscript in preparation.

(9) Ripmeester, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 289.

(10) Fowler, P. W.; Lazzaretti, P.; Zanasi, R. *Chem. Phys. Lett.* **1990**, *165*, 79.

(11) Benedek, G. B.; Englman, R.; Armstrong, J. A. *J. Chem. Phys.* **1963**, *39*, 3349.

(12) Jameson, C. J.; Rehder, D.; Hoch, M. *J. Am. Chem. Soc.* **1987**, *109*, 2589.

(13) Jameson, C. J.; Osten, H. J. *Annu. Rep. NMR Spectrosc.* **1986**, *17*, 1 and references therein.

(14) Ditchfield, R. *Chem. Phys.* **1981**, *63*, 185.

(15) Chestnut, D. B. *Chem. Phys.* **1986**, *110*, 415; *Annu. Rep. NMR Spectrosc.* **1989**, *21*, 51 and references therein.

(16) Jokisaari, J.; Raisanen, K. *Mol. Phys.* **1978**, *36*, 1113. Jokisaari, J.; Raisanen, K.; Lajunin, L.; Passoja, A.; Pyykkö, P. *J. Magn. Reson.* **1978**, *31*, 121.

(17) Harris, S. Bradley, J. S. *Organometallics* **1984**, *3*, 1086. Benson, C. G.; Long, G. J.; Bradley, J. S.; Kolis, J. W.; Shriver, D. F. *J. Am. Chem. Soc.* **1986**, *108*, 1898. Halet, J.-F.; Evans, D. G.; Mingos, D. M. P. *J. Am. Chem. Soc.* **1988**, *110*, 87. Wales, D. J.; Stone, A. J. *Inorg. Chem.* **1989**, *28*, 3120. See also: Wijeyesekera, S. D.; Hoffman, R. *Organometallics* **1984**, *3*, 949.

(18) Brint, P.; O'Cuill, K.; Spalding, T. R. *Polyhedron* **1986**, *5*, 1791.

(19) Groombridge, C. J.; Larkworthy, L. F.; Mason, J. To be published.