ELSEVIER

Catalysis Today 50 (1999) 669–675

CATALYSIS TODAY

Insights into homogeneous catalysis from first-principles theory: density functional studies of inorganic cobalt complexes

D.J. Doren*, R. Konecny[1], K.H. Theopold

Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716, USA

Abstract

Density functional theory (DFT) has been used to predict geometries, energies and spin states of a series of inorganic cobalt complexes containing the geometry-constraining Tp (tris(pyrazolyl borate)) ligand. For example, the carbonyl, TpCoCO, is a stable 16-electron compound with an unusual asymmetric geometry. This molecule is the structural and electronic analog of an unstable intermediate in C–H bond activation. DFT studies of TpCoCO permit detailed comparisons of theory to experiment, and a rationale for the structure that applies to unstable species as well. More recent work has focused on reactive molecules, including $(TpCo)_2O_2$ complexes (with 36 heavy atoms) that may be useful in catalyzing alkane oxidation. DFT provides a useful guide to the feasibility of proposed oxidation mechanisms.

Keywords: DFT; First-principles theory; Cobalt complexes

1. Introduction

Large transition metal complexes present significant challenges to first-principles theory. Since many molecular properties can be understood from qualitative arguments or semi-empirical theories, the primary role of first-principles theory is to understand subtle cases and make detailed predictions. Given their substantial computational cost, first-principles methods can only be useful if they make predictions that are reliably more accurate than those of simpler theories. Bonding to transition metals is quite subtle, and an accurate theory must include electron correlation effects. However, traditional post-Hartree–Fock methods cannot be applied to large molecules at an affordable cost. Density functional theory (DFT) methods are a promising class of methods for such problems, which include electron correlation at a cost comparable to Hartree–Fock theory. DFT methods have been thoroughly tested for small molecules and the so-called non-local methods generally predict structures and bond energies to an accuracy comparable to that of second-order Møller–Plesset perturbation theory (MP2, a post-Hartree–Fock method). However, the reliability of DFT for transition metal complexes is not so well documented. In particular, for paramagnetic complexes, where several spin states may have comparable energies, it is not certain that DFT methods can predict the correct ground electronic state.

We have been applying DFT to a series of large inorganic molecules with novel bonding patterns, many of which are paramagnetic. The work described here illustrates the accuracy of DFT in inorganic

---

*Corresponding author. Tel.: +1-302-831-1070; fax: +1-302-831-6335; e-mail: doren@udel.edu

[1] Present Address: Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, NY 14853-1301, USA.

0920-5861/99/$ – see front matter
PII: S0920-5861(98)00501-X

complexes that have practical interest for understanding catalytic chemistry. Many of the molecules studied have experimentally determined structures and/or reactivities, which provide tests of the DFT predictions of structure and energetics. The success of DFT in the cases where experimental data are available is encouraging, and provides some confidence for using this theory to understand molecules that are not stable, are not accessible to the full range of structural measurements, or whose existence is merely postulated.

2. TpCo–L complexes (Tp=tris(pyrazolyl) borate)

The molecules described in this paper involve Co atoms coordinated by a tris(pyrazolyl) borate ligand, abbreviated as Tp and illustrated in Fig. 1. In this section, we shall describe complexes with one additional ligand, L, bound to Co. The Tp ligand is isoelectronic with cyclopentadienyl (Cp), having a formal charge of -1, which helps to stabilize the charge on metal atoms with high oxidation states [1,2]. Tp ligands with bulky R groups (such as isopropyl or *t*-butyl) are known as "tetrahedral enforcers" [1,2]. They enforce four-fold coordination around Co through steric constraints, allowing only one additional ligand, L. We let R=H throughout the theoretical treatment, as this is expected to have little effect on ligand structure, energetics or electronic states. However, in some applications this may not be an adequate approximation (vide infra).

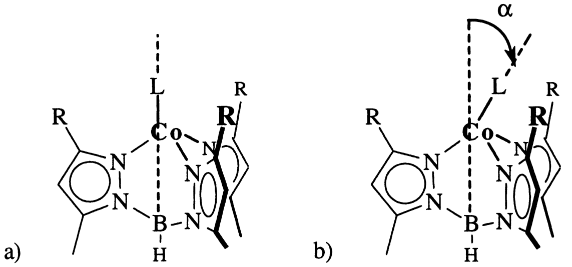


Fig. 1. Structures of TpCo–L (Tp=tris(pyrazolyl) borate) complexes. (a) indicates a "linear" structure, in which the ligand L lies on the symmetry axis of Tp. (b) indicates a "bent" structure in which the ligand L is displaced from the C_3 symmetry axis by an angle α.

TpCo complexes illustrate the challenge to theory described above. Bonding to a transition metal requires a reasonable treatment of electron correlation for reliable predictions of energetics, though the size of the molecule (the TpCo fragment has 17 heavy atoms) makes traditional post-Hartree–Fock methods quite expensive for geometry optimization. One could replace the Tp ligand with smaller model ligands, but we were concerned that small models could not reproduce the forces in the Tp cage or the aromatic electronic environment of the pyrazole rings. Such differences may be important for accurate predictions of geometry. For example, X-ray structures of some TpCo–L complexes show that the three Co–N bonds may differ from each other over a range of almost 0.1 Å [3]. We shall show that Co–N bond lengths are quite sensitive to the spin state, and failure to predict these bond lengths accurately is often an indication that the wrong electronic state is being studied. A useful model must reproduce the Co–N bond lengths, so that few simplifications in the Tp ligand are possible. With current DFT technology we are able to fully optimize TpCo complexes including electron correlation effects. We shall show that this approach produces accurate geometrical predictions, and no constraints or assumptions about geometry are required.

An alternative approach has been used in recent work by Canty et al. [4]. They have applied Hartree–Fock and MP2 theory to model complexes where the pyrazole rings were replaced by smaller structures that maintain the basic cage structure of the Tp ligand. The main difference between this model and Tp appears to be loss of conjugation in the pyrazole rings. The number of heavy atoms in the TpCo fragment is reduced from 17 to 11, and it is feasible to optimize the model complex with MP2 theory.

2.1. L=CO

TpCoCO provides an interesting example with relevance to alkane activation catalysis. This 16-electron, Co(I) (d^8) coordinatively unsaturated complex is analogous to (and isoelectronic with) Cp^*MCO ($Cp^*=\eta^5$-C_5Me_5, M=Rh, Ir), a highly reactive intermediate which adds unactivated C–H bonds of alkanes [5–11]. Since TpCoCO is stable, it provides an opportunity for understanding a structural choice in the more reactive chemical analog. The TpCo structure has three-fold symmetry, yet initial X-ray diffraction studies indicated that the carbonyl ligand does not lie on the symmetry axis (Fig. 1(b)) [3]. However, the first X-ray study of TpCoCO could not resolve the details of the carbonyl structure due to disorder problems. This left some open questions, such as whether Co and the CO bond were collinear, and the physical origin of this symmetry lowering.

Initial calculations with a local spin density functional showed that a bent structure, with Co, C and O collinear, was more stable than the optimal structure with C_{3v} symmetry. However, the Co–N bonds were shorter than the value obtained from X-ray diffraction by almost 0.1 Å. This error is too large for a chemically accurate theory. The Becke–Perdew non-local spin density (NLSD) functional was used to refine the geometry, giving the result shown in Fig. 2. The NLSD structure has longer Co–N bonds and the bent structure (bending angle α=27.7°, with respect to the C_{3v} axis) is again more stable than the optimal C_{3v} structure. Moreover, while this calculation was being performed, a new X-ray structure was completed that is in excellent agreement with the structure predicted from NLSD; the measured bend angle is α=26.6° and all the bond lengths agree with the calculated structure within 0.03 Å (excluding bonds to hydrogen, which are systematically too short in X-ray structures) [3]. Thus, the NLSD theory can accurately predict geometries of these complexes.

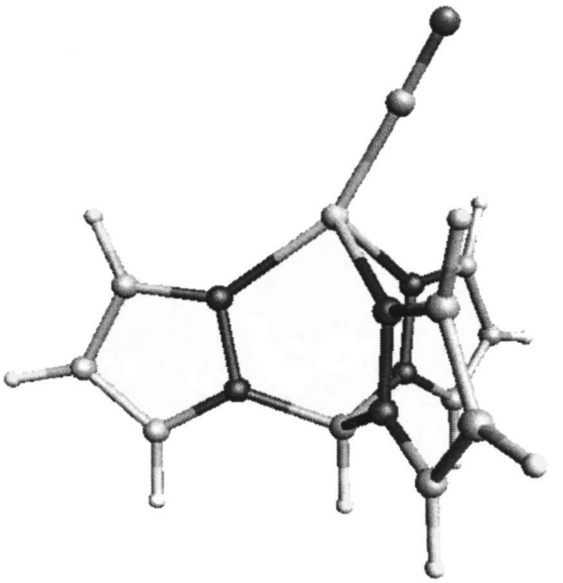


Fig. 2. The DFT-optimized (Becke–Perdew functional) structure of TpCoCO in its ground (triplet) electronic state. The structure has a single C_s symmetry plane. Selected structural parameters (predicted values followed by corresponding values from X-ray diffraction in parentheses): Co–C, 1.79 Å (1.77 Å); C–O, 1.18 Å (1.15 Å); Co–N, 2.02 Å (2.04 Å); α, 27.7° (26.6°); Co–C–O, 176.0° (177.8°).

The physical origin of the carbonyl bending can be understood from elementary bonding considerations. In fact, the basic argument was developed 15 years ago for CpCoCO by Hofmann and Padmanabhan [12], using extended Hückel theory (EHT). The three highest occupied EHT orbitals for TpCoCO are shown at the linear (C_{3v}) and bent (optimal) geometries in Fig. 3, along with an EHT Walsh diagram which shows how the energy of the MO's derived from Co d-orbitals change with the bending angle, α. The driving force for bending is reduction of an antibonding interaction between the C-based lone pair orbital of CO and the Co d_{z^2} orbital in the 2a′ MO. This is balanced by loss of a favorable π interaction in the 3a′ MO.

The effect of bending on the total energy can be inferred from the Walsh diagram if the spin state is known. However, EHT does not account for exchange interactions and cannot predict the lowest energy spin state. For this d^8 complex, the degeneracy of the HOMO in the linear geometry implies that this geometry must have a triplet ground state. The DFT calculations predict that the ground state is also a triplet in the optimal bent configuration, in agreement with magnetic moment measurements [3]. The lowest triplet state corresponds to a $(2a')^2(2a'')^1(3a')^1$ configuration. This means that the optimal bending angle is determined by a competition between the stabilization of the doubly occupied 2a′ orbital and the destabilization of the singly occupied 3a′ orbital. The contribution of the doubly occupied orbital dominates at small angles. EHT predicts an optimal angle of α=32°, which is remarkably similar to the experimental value. Note that a singlet ground state configuration would bend to a much larger angle as the 3a′ orbital is not occupied.

Based on their EHT calculations, Hofmann and Padmanabhan argued that a bent geometry could stabilize a singlet state for d^8 molecules of the type

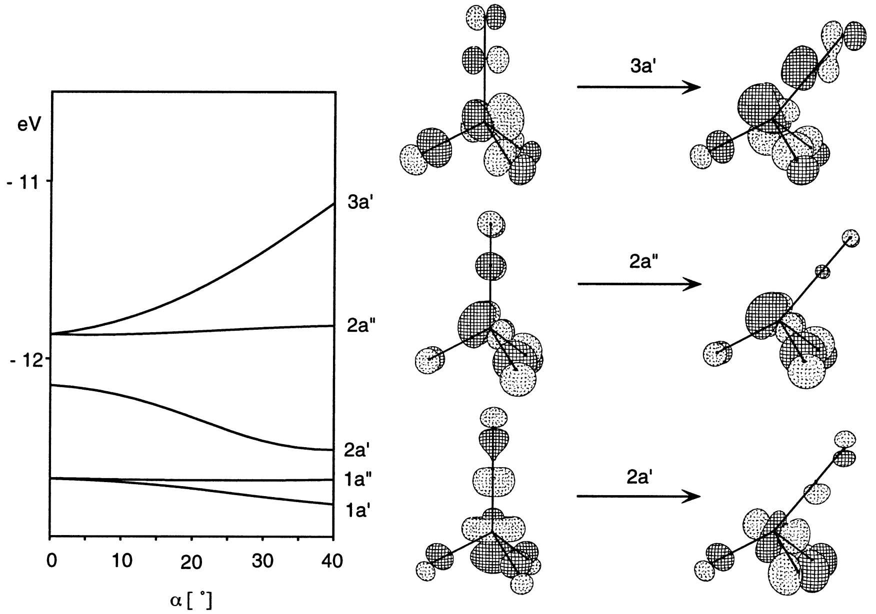


Fig. 3. Changes in the EHT orbitals of TpCoCO as a function of the angle α. The Walsh diagram indicates energies of the occupied orbitals involving Co d-functions; the three highest energy orbitals are shown at the linear (α=0°) and optimal EHT (α=32°) geometries.

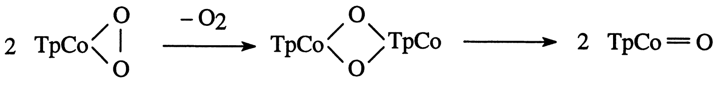
CpCoL [12]. Because EHT cannot predict the relative energy of different spin states, they were not able to determine the geometry at which the singlet becomes lower in energy than the triplet. The present work shows, in the isoelectronic case of TpCoCO, that a singlet state can only be more stable than a triplet at angles α significantly greater than 30°.

2.2. *L=I*

Application of DFT to TpCoI further illustrates the capabilities of the method. The Walsh diagram for this molecule is qualitatively similar to that of the carbonyl in Fig. 3. However, the iodide is a Co(II) (d^7) complex, so its configuration will be either $(2a')^2(2a'')^1$ (for a doublet ground state) or $(2a')^1(2a'')^1(3a')^1$ (for a quartet). Such a doublet would be degenerate in the linear configuration, so it would undergo a first-order Jahn–Teller distortion to a bent structure. On the other hand, the quartet geometry is determined by a delicate balance between the singly occupied 2a′ and 3a′ orbitals, which does not favor significant bending. Local spin density calculations show that the doublet and quartet have similar energies, though the doublet is slightly favored. In contrast, non-local spin density calculations show that the (nearly linear, α=4°) quartet is favored by about 23 kcal/mol over the (slightly bent, α=10°) doublet. Again, the Co–N bond lengths are quite sensitive to both the functional used and the spin state. In the doublet, the Co–N bond lengths are predicted to be 0.08 Å shorter than in the quartet by both local and non-local functionals. Experiments are in close agreement with the predictions of NLSD for the quartet; the predicted and X-ray structures are nearly identical, and magnetic moment measurements are consistent with a quartet [3].

3. Oxygen activation: $(TpCo)_2O_2$ and related complexes

The success of DFT in predicting structures has motivated predictions of the properties of molecules that have not been structurally characterized. An example is the $(TpCo)_2O_2$ complex. This molecule, and similar species have been synthesized to study their possible role in oxidation catalysis [13]. The synthesis can be accomplished by exposing TpCoCO to O_2 to form a Co(II) dioxygen complex, $TpCoO_2$, in which the dioxygen is bound side-on to the metal atom and the O–O bond remains intact. These molecules dimerize and lose O_2 to form a binuclear complex. If the O–O bond is cleaved in these complexes (Eq. (1)), dissociation may occur to form metal oxo (M=O) species that are analogous to oxidizing species in some enzymatic reactions [14]. If the metal oxo reacts with a substrate to reduce the metal, a complete catalytic cycle is possible.



(1)

Schemes such as this for activating dioxygen are essential for selective oxidation chemistry. Since oxygen is a readily available strong oxidant, it is the preferred source of oxygen atoms for large-scale commercial reactions. However, the large kinetic barriers and low selectivities of typical reactions of O_2 imply that this molecule must be "activated," or incorporated into a reactive, yet selective reagent, if it is to be synthetically useful.

Quantitative first-principles theory can provide a useful complement to the experimental work on these complexes. $(TpCo)_2O_2$ is so reactive that direct structural determinations have not been possible. The first question is whether the O–O bond remains intact in the complex. Some related copper complexes provide precedents for both intact and broken O–O bonds. Kitajima and co-workers [15–17] have characterized a binuclear Cu complex of the type $(TpCu)_2(\mu\text{-}O_2)$, with an intact O–O bond. Studies by Tolman and co-workers [18–21] on analogous binuclear Cu complexes have established that structures with broken and intact dioxygen bonds ($(\mu\text{-}O)_2$ and $(\mu\text{-}O_2)$, respectively) are close in energy and can be interconverted easily. One expects somewhat different chemistry for Co, with a preference for high oxidation states that favor O–O bond cleavage.

Efforts to obtain an X-ray structure for $(TpCo)_2O_2$ have not yet been successful, so we have used DFT to determine structures for $(TpCo)_2O_2$ and related species. These calculations use the B3-LYP hybrid theory, which mixes a non-local density functional with an added "exact" exchange energy. This method generally gives better estimates of exchange interactions than LSD or the Becke–Perdew functional used for the TpCoL complexes. One subtlety of these calculations is that each molecule has several potential spin states for which independent calculations of optimal geometries and energies must be done.

The calculated structure for $(TpCo)_2O_2$ is shown in Fig. 4. This bis(μ-oxo) structure clearly has a cleaved O–O bond, with the oxygen atoms separated by 2.48 Å. To estimate the energy difference between this structure and a $(\mu\text{-}O_2)$ structure, we have also optimized the geometry with the O–O bond constrained to 1.4 Å. The energy of the constrained structure is almost 40 kcal/mol higher than the bis(μ-oxo) structure, and optimization from the optimal structure with a short O–O bond proceeds directly to a bis(μ-oxo) structure. This is in clear contrast to the Cu analogs synthesized by Tolman, where O–O bond cleavage is reversible and theoretical predictions by

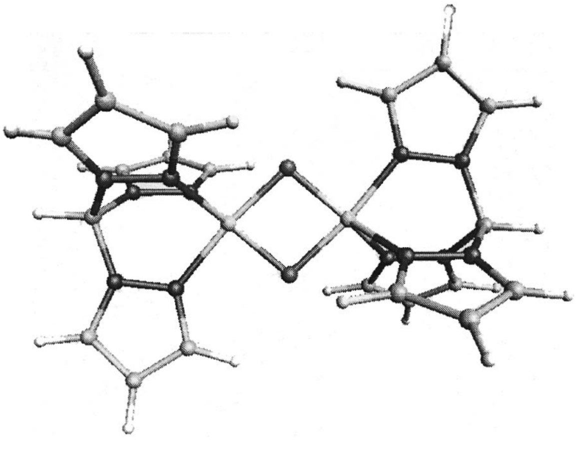


Fig. 4. B3-LYP optimized bis(μ-oxo) structure of $(TpCo)_2O_2$ in its ground electronic state. The structure has an inversion center, but no other symmetry elements. The ground state is predicted to be a quintet, corresponding roughly to two metal centers in triplet states, coupled together ferromagnetically into a quintet. Selected structural parameters: Co–O, 1.845 and 1.848 Å; O–O, 2.401 Å; Co–Co, 2.802 Å; Co–N, 1.969, 2.072 and 2.078 Å; Co–O–Co, 98.7°; O–Co–O, 81.1°.

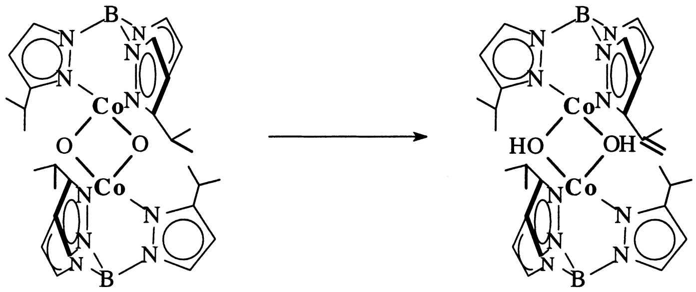


Fig. 5. The (μ-O)$_2$ complex rapidly abstracts H from the isopropyl substituents on the Tp ligand at room temperature to form a (μ-OH)$_2$ complex.

Cramer et al. [21] show that there are minima corresponding to both the (μ-O)$_2$ and (μ-O$_2$) structures with similar energies.

Theory can also provide some tests of proposed reaction mechanisms. For example, the mononuclear metal oxo intermediate in the proposed alkane oxidation mechanism described above must be formed by homolytic dissociation of (TpCo)$_2$O$_2$ (Eq. (1)). However, this dissociation step is predicted to be strongly endothermic, with a reaction energy of over 41 kcal/mol. Hence, it is unlikely that oxidation can occur through the proposed mechanism. Nevertheless, (TpCo)$_2$O$_2$ appears to be a strong oxidant. The molecules as synthesized have substitutions on the pyrazole rings, R=isopropyl, and hydrogen is rapidly abstracted from the isopropyls at room temperature to form a bis(μ-hydroxo) complex, (TpCo)$_2$(OH)$_2$ (Fig. 5). Our calculations predict that the first O–H bond formed has an energy of only 95 kcal/mol (not including the zero point energy, which will lower the bond dissociation energy by 4–5 kcal/mol), while the second one has a bond energy of 107 kcal/mol. The first weak O–H bond is consistent with the observation that abstraction of hydrogen from tertiary C–H bonds is activated, and does not occur at reduced temperature [13]. However, the average of the two O–H bond energies (101 kcal/mol, without zero point energy) is high enough that we expect hydrogen abstraction to be thermodynamically favored, even from primary C–H bonds. Nevertheless, the modest O–H bond strengths may allow for some selectivity in oxidation of alkanes.

The (μ-OH)$_2$ complex can be isolated and its structure has been characterized by X-ray diffraction. This provides an important test of the theory for these binuclear complexes. As might be expected, a rich set of spin states must be explored. Similar to the TpCoI complex, the Co–N bond lengths are sensitive to the spin state. The lowest lying state is predicted to be a septet with three unpaired spins on each metal center. Magnetic moment measurements show that the complex behaves as two uncoupled quartets. This appears to be consistent with our predicted spin state, which can be described as two quartets, weakly coupled into a septet. The geometry of the septet state agrees reasonably well with the X-ray structure, but there are some significant errors. For example, the Co–N bonds that lie in the Co–O–O–Co plane is too short by 0.07 Å. Nevertheless, all other spin states studied have more dramatic errors in the geometry, underestimating the Co–N bond lengths by more than 0.15 Å. While this comparison provides some evidence that the hybrid B3-LYP method can provide reliable predictions for both the geometry and spin states of these binuclear complexes, the agreement with experiment is not as good as in the other examples studied and the reasons for this remain to be understood. One possibility is that steric interactions between the hydroxyls and the isopropyl substituents on the pyrazole rings (which are neglected in the present calculations) lead to strain on the Co–N bonds that lie in the Co–O–O–Co plane. Direct calculations of the geometry for models that include isopropyl substituents are now feasible with non-local DFT, and we plan to explore the effects of substituents on geometry and energetics.

Before a (TpCo)$_2$O$_2$ complex can be a useful reagent for selective oxidation, it must be prevented from abstracting hydrogen from its own ligands. This is one of the current challenges to synthetic work on these molecules, but theory provides some guidance. Given the predicted O–H bond energies, it may be possible to slow the abstraction reaction by using substituted Tp ligands that place only strong C–H bonds in the vicinity of O. Current synthetic work is pursuing this direction.

4. Conclusions

Density functional methods can now make accurate predictions of structure and energetics in systems with 30 or more heavy atoms. This makes it possible to apply first-principles methods to the same inorganic molecules used in laboratory work, rather than artificial model compounds. Predictions of geometry, spin states and relative energetics are in excellent agreement with experiment. Studies of catalytically active intermediates that cannot be experimentally characterized provide especially attractive applications of these methods, though at present we regard predictions about such molecules as a guide to further work, rather than as definitive results.

The work described here illustrates the capabilities of various theoretical approaches to large inorganic complexes. While local spin density functionals often provide a reasonable approximation to the geometry of TpCo complexes, significant errors in bond lengths occur in some cases. Moreover, local DFT can predict the wrong spin for the ground state. On the other hand, non-local density functionals with a modest basis set consistently predict accurate geometries and spin states in the examples that we have surveyed. Simple models based on EHT can provide a useful qualitative guide for understanding the physical origins of structural choices. However, EHT cannot predict the spin of the ground state, so some additional information about the spin state, from DFT or experiment, is needed to apply to the model.

Acknowledgements

The research reported here has been supported by the National Science Foundation (CHE-9401312 and CHE-9708363 to DJD) and the US Department of Energy (ER14273 to KHT).

References

[1] S. Trofimenko, J.C. Calabrese, J.S. Thompson, Inorg. Chem. 26 (1987) 1507.
[2] S. Trofimenko, Chem. Rev. 93 (1993) 943.
[3] J.L. Detrich, R. Konecny, W.M. Vetter, D. Doren, A.L. Rheingold, K.H. Theopold, J. Am. Chem. Soc. 118 (1996) 1703.
[4] A.J. Canty, A. Dedieu, H. Jin, A. Milet, M.K. Richmond, Organometallics 15 (1996) 2845.
[5] A.H. Janowicz, R.G. Bergman, J. Am. Chem. Soc. 104 (1982) 352.
[6] J.K. Hoyano, W.A.G. Graham, J. Am. Chem. Soc. 104 (1982) 3723.
[7] J.K. Hoyano, A.D. McMaster, W.A.G. Graham, J. Am. Chem. Soc. 105 (1983) 7190.
[8] A.H. Janowicz, R.G. Bergman, J. Am. Chem. Soc. 105 (1983) 3929.
[9] W.D. Jones, F.J. Feher, J. Am. Chem. Soc. 106 (1984) 1650.
[10] R.G. Bergman, Science 223 (1984) 902.
[11] W.D. Jones, F.J. Feher, Acc. Chem. Res. 22 (1989) 91.
[12] P. Hofmann, M. Padmanabhan, Organometallics 2 (1983) 1273.
[13] O.M. Reinaud, K.H. Theopold, J. Am. Chem. Soc. 116 (1994) 6979.
[14] S.J. Lippard, J.M. Berg, Principles of Bioinorganic Chemistry, University Science Books, Mill Valley, CA, 1994, p. 302 ff.
[15] N. Kitajima, K. Fujisawa, Y. Moro-oka, J. Am. Chem. Soc. 111 (1989) 8975.
[16] N. Kitajima, T. Koda, Y. Iwata, Y. Moro-oka, J. Am. Chem. Soc. 112 (1990) 8833.
[17] M.J. Baldwin, D.E. Root, J.E. Pate, K. Fujisawa, N. Kitajima, E.I. Solomon, J. Am. Chem. Soc. 114 (1992) 10421.
[18] S. Mahapatra, J.A. Halfen, E.C. Wilkinson, G. Pan, C.J. Cramer, L. Que Jr., W.B. Tolman, J. Am. Chem. Soc. 117 (1995) 8865.
[19] J.A. Halfen, S. Mahapatra, E.C. Wilkinson, S. Kaderli, V.G. Young Jr., L. Que Jr., A.D. Zuberbühler, W.B. Tolman, Science 271 (1996) 1397.
[20] S. Mahapatra, J.A. Halfen, W.B. Tolman, J. Am. Chem. Soc. 118 (1996) 11575.
[21] C.J. Cramer, B.A. Smith, W.B. Tolman, J. Am. Chem. Soc. 118 (1996) 11283.