© 2002 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 75, 1657–1679 (2002)

Accounts

Inorganic Chemistry Based on Tp Ligands —From Dioxygen Complexes to Organometallic Systems—

Munetaka Akita* **and Shiro Hikichi**[#]

Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503

(Received November 13, 2001)

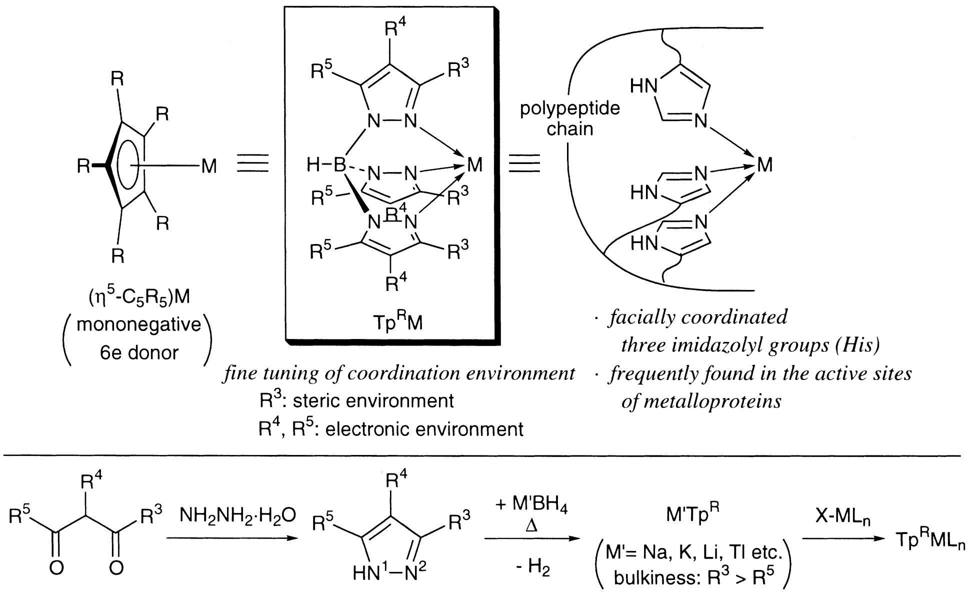
Our recent research on transition metal complexes containing hydrotris(pyrazolyl)borato ligands (Tp^R), which ranges from bioinorganic chemistry of dioxygen complexes to organometallic systems, is reviewed. The Tp^R ligand turns out to be versatile in a wide variety of inorganic studies, because the coordination properties (both steric and electronic) can be finely tuned in a systematic manner by choosing appropriate substituents on the pyrazolyl rings to serve the purpose of the study (e.g. stabilization, activation, functionalization). For first row transition metal complexes, Tp^R serves as a tetrahedral enforcer to form a coordinatively unsaturated tetrahedral species, which is interconverted with five- and six-coordinate structures via coordination/dissociation of donor(s). In addition to the traditional view of Tp^R as a ligand system isoelectronic with cyclopentadienyls (η^5-C_5R_5), the Tp^R ligand is now recognized as a unique ancillary ligand suitable for bioinorganic studies, because the tripodal ligand can mimic the coordination environment created by three imidazolyl groups from histidine residues, which is frequently found in the active sites of metalloenzymes. Through extension of the metal in Tp^RM-O_2 adducts to those not related to biological systems we have unveiled the following new aspects of the chemistry of transition metal dioxygen complexes: (1) formation of higher valent bis(μ-oxo) species, $Tp^RM(\mu\text{-}O)_2MTp^R$ (M = Co, Ni), via O–O cleavage of $Tp^RM(\mu\text{-}\eta^2:\eta^2\text{-}O_2)MTp^R$ intermediates and their relevance to the active intermediate of *methane monooxygenase*, (2) formation and full characterization of a variety of peroxo, hydroperoxo (Pd, Rh) and alkylperoxo species (Mn, Co, Ni, Pd), (3) structural evidence for conversion of molecular oxygen into hydroperoxide via protonation of the η^2-peroxo intermediate (Rh), and (4) formation of an active species which undergoes oxidative C–C cleavage reaction (Ru). The property of the Tp^R ligand as a tetrahedral enforcer is best demonstrated in organometallic systems. The hydrocarbyl complexes, Tp^RM-R' (M= Fe, Co), are stable with respect to thermal decomposition processes involving β-hydrogen elimination despite their highly coordinatively unsaturated electronic structure [Fe(14e), Co(15e)], when they are kept under inert atmosphere. The stability has been ascribed to a high spin configuration caused by the tetrahedral geometry. All frontier orbitals are occupied by unpaired electrons or electron pairs and no vacant frontier orbital is left for interaction with the electron pairs of a donor. Dinuclear xenophilic complexes, Tp^RM–$M'L_n$, with a polar metal–metal bond which bridges a Werner complex type hard open-shell metal center and a coordinatively saturated metal carbonyl fragment are also synthesized and fully characterized.

Hydrotris(pyrazolyl)borates (Tp^R; Scheme 1) were first synthesized and reported by Trofimenko in 1966.[1,2] They are a versatile class of auxiliary ligands for study of inorganic chemistry of transition metals and main group elements.[3,4] Although the Tp^R ligand can be coordinated to a metal center in κ^3- to κ^0-fashion,[5] it has been mainly used to create a κ^3-coordination environment and is therefore nicknamed "scorpionate"; the κ^3-binding mode resembles the shape of a hunting scorpion (with the two claws and the tail).[6]

The features of the Tp^R ligand revealed by the previous studies can be summarized as follows. (1) Despite the apparently complicated structure the Tp^R ligand can be readily prepared by thermal dehydrogenative condensation between a BH_4- salt and pyrazole,[1b] which is also readily obtained by condensation of 1,3-diketone with hydrazine hydrate. (2) The coordination behavior of the Tp^R ligand can be finely tuned in a systematic manner by introduction of appropriate substituents (R^{3-5}) onto the pyrazolyl rings. Because, at the stage of the synthesis of the Tp^R salt ($M'Tp^R$), the more bulky substituent of the R^3 and R^5 groups of the pyrazole occupies the R^3 position to relieve the steric repulsion among the substituents at the R^5 positions, the 3-substituents (R^3) proximal to the metal center in the resulting Tp^RML_n complexes control the steric environment around the metal center, and the cone angles of Tp^R ligands exceed 180°.[7] On the other hand, the electronic environment at the metal center can be adjusted by introduction of electron-releasing or -withdrawing groups at the 4- and/or 5-positions

---

[#] The present address: Department of Applied Chemistry, School of Engineering, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656



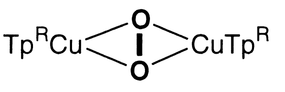
Scheme 1.

($R^{4,5}$). The R^5 groups also control the coordination property of the nitrogen atoms (N–M–N bite angles); i.e. steric repulsion among bulky R^5 substituents would bring the coordinating nitrogen atoms (N^2) close together to tightly bind the metal center. (3) The Tp^R ligand has been recognized as a "tetrahedral enforcer" of first row transition metal species and leads to low-coordinate, coordinatively unsaturated species [in particular, tetrahedral species (κ^3-Tp^R)M–L], which usually have a high spin electronic configuration. Steric protection of the metal center by bulky R^3 groups should also contribute to kinetic stabilization of low-coordinate species.

Despite these advantageous features the Tp^R ligand also has a couple of drawbacks. The simple synthetic procedure hampers selective synthesis of an unsymmetrically substituted derivative, $HB(pz^Rpz^{R'}pz^{R''})$, including a chiral one. In principle, different pz^R groups could be introduced in a stepwise manner, but the thermal condensation at the final stage (> 150 °C) causes redistribution of the pz^R groups to give a mixture of products, separation of which is difficult due to the ionic and hydrolysable nature of Tp^R. In some cases, chromatographic separation may be applicable after conversion to stable derivatives (e.g. Tp^RTl). In addition, synthesis of half-sandwich complexes (Tp^RL_nM-X) containing a functionalizable group (X) is not always facile, because reactions of MX_2L_n with Tp^R anion may lead to the formation of the kinetically inert ferrocene-like sandwich complexes $(Tp^R)_2M$. But this problem can be overcome in some cases by using a bulky Tp^R ligand or a bidentate anion (κ^2-X).[8]

The κ^3-Tp^R ligand, a mononegative 6e-donor, is isoelectronic with η^5-cyclopentadienyl ligands (η^5-C_5R_5), which have been widely used as auxiliary ligands of organometallic compounds, and therefore many comparative studies of the related Tp^RML_n and (η^5-C_5R_5)ML_n systems have been carried out. The previous studies have revealed that (1) Tp^R renders the metal center harder than η^5-C_5R_5 does, (2) Tp^R causes smaller ligand field splitting [cf. $Fe(Tp^H)_2$: paramagnetic vs $Fe(\eta^5\text{-}C_5H_5)_2$: diamagnetic],[9] and (3) Tp^R is a better π-donor [cf. ν_{CO} for $Tp^RM(\equiv CR')(CO)_2$ and (η^5-C_5R_5)$M(\equiv CR')(CO)_2$ (M = Mo, W)].[10] These properties, in principle, should result from the different energy levels of the atomic orbitals of the coordinating atoms, i.e. the AOs of N are lower in energy than those of C and the AOs of C are closer to those of metal d orbitals so as to form interactions with more covalent character.

In contrast to these traditional views of the Tp^R ligand, the Tp^R ligand system is anticipated to mimic the coordination environment created by the facially arranged three imidazolyl groups which are involved in the histidine residues, and such a structural motif is frequently found in the active sites in metalloproteins (Scheme 1). Kitajima and Moro-oka first recognized this feature when they attained a new phase of bioinorganic chemistry based on the Tp^RM systems as typically exemplified by the significant contribution of the study on the Tp^RCu-O_2 adducts to elucidation of the O_2-coordination mode in *oxyhemocyanin*.[11] It had been known that *hemocyanin* (the O_2-transport copper protein of mollusks, arthropods and invertebrates) contained a dicopper O_2-binding site and that each metal center was located exactly in the above-mentioned coordination environment with the facially arranged three imidazolyl groups but the O_2-coordination mode in *oxyhemocyanin* (the O_2-adduct of *hemocyanin*) had remained a matter of controversy. A number of model compounds for *oxyhemocyanin* had been prepared but none of them could reproduce its spectroscopic features satisfactorily (in particular, the low $\nu_{O\text{-}O}$ vibration appearing around 750 cm^{-1}). The dicopper complex $Tp^{iPr_2}Cu(\mu\text{-}\eta^2{:}\eta^2\text{-}O_2)CuTp^{iPr_2}$ $\mathbf{1a}^{Cu}$ (Chart 1)[12,13] prepared in the laboratory of Kitajima and Moro-oka exhibited the spectroscopic features closely resembling to those of *oxyhemocyanin* and, on the basis of its X-ray structure, they predicted the μ-



$\mathbf{1}^{Cu}$

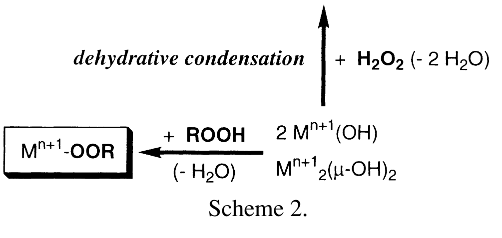
Chart 1.

$\eta^2:\eta^2$-coordination of the dioxygen molecule, which was later verified by the crystallographic study of the *oxyhemocyanin* isolated from *Limulus polyphemus*.[14] This work has also been regarded as a successful example of bioinorganic study using a well-characterized low-molecular weight model compound.[15]

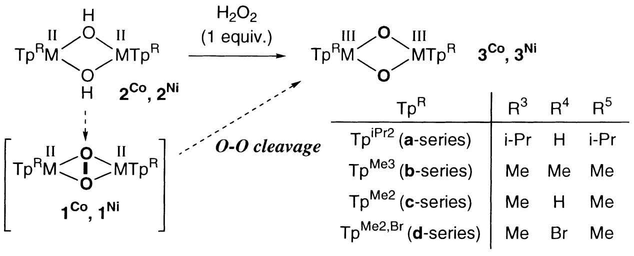
The present research has been carried out as an extension of the above-mentioned bioinorganic study of Tp^RM-dioxygen complexes to more general inorganic chemistry. If we could prepare a series of $Tp^RM(\mu$-"O_2"$)MTp^R$- and $Tp^RM($"O_2"$)$-type transition metal-dioxygen complexes, where the Tp^RM moiety has the similar structural features but is different in the number of d-electrons and the energy levels of d-orbitals, we would be able to directly evaluate the electronic effect of the central metal on the structure and reactivity of the resultant "dioxygen" complexes.[16] Metal-coordinated dioxygen species have been regarded as key intermediates of catalytic O_2-oxygenation reactions,[16] which attract much attention from not only the biological but also the synthetic viewpoints. Our work employing some central metals irrelevant to the biological systems has led to the discovery of new types of "dioxygen" complexes including the high-valent bis(μ-oxo) complexes $[Tp^RM(\mu\text{-}O)_2MTp^R]$, although such an attempt has not been always successful. In this *Account* we will describe the results obtained in our laboratory on (1) a series of first- and second-row transition metal dioxygen complexes and related M-OOR complexes and (2) unusual organometallic systems arising from the unique properties of the Tp^R ligand featured as "tetrahedral enforcer".

1. First Row Transition Metal Dioxygen Complexes

1.1. Dinuclear Bis(μ-oxo) Complexes of Cobalt and Nickel.[17] Dinuclear dioxygen complexes including the dicopper(II)-dioxygen complex $\mathbf{1^{Cu}}$ (Chart 1) can be accessible via two synthetic routes, i.e. (i) oxidative addition of an O_2 molecule to two molecules of a low valent precursor and (ii) dehydrative condensation between a hydroxo complex and H_2O_2 (Scheme 2).[11] The second method developed in our laboratory is complementary to the classical oxidative addition method (i) and has the advantages that (1) dioxygen complexes can be obtained for the metal systems where low valent precursors are not available and (2) the method can be applied to the synthesis of mononuclear alkyl- and hydroperoxo complexes, M-OOR (R = alkyl, H), by condensation with the corresponding ROOH reagents (see sections 1.2. and 2.). Fortunately, for the Tp^RM systems, we could obtain a series of dinuclear divalent di(μ-hydroxo) complexes of first row transition metals, $Tp^RM^{II}(\mu\text{-}OH)_2M^{II}Tp^R$ **2** (M = Cr, Mn, Fe, Co, Ni, Cu),[18] each of which was subjected to the dehydrative condensation with H_2O_2. As a result, new type dioxygen complexes were obtained for the Co and Ni systems, whereas the reactions of the Cr, Mn and Fe complexes resulted in oxidation of the central metals to give M^{III} species.[19]



Scheme 2.



Tp^R	R^3	R^4	R^5
Tp^{iPr2} (**a**-series)	i-Pr	H	i-Pr
Tp^{Me3} (**b**-series)	Me	Me	Me
Tp^{Me2} (**c**-series)	Me	H	Me
$Tp^{Me2,Br}$ (**d**-series)	Me	Br	Me

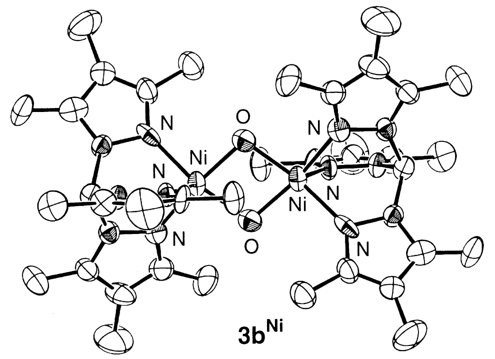
Scheme 3.

1.1.1. Synthesis and Characterization.[2] Treatment of the hydroxo complexes of cobalt ($\mathbf{2^{Co}}$) and nickel ($\mathbf{2^{Ni}}$) with an equimolar amount of H_2O_2 (30% aqueous solution) at −78 °C afforded thermally unstable dark brown species $\mathbf{3^{Co}}$ and $\mathbf{3^{Ni}}$ (Scheme 3).

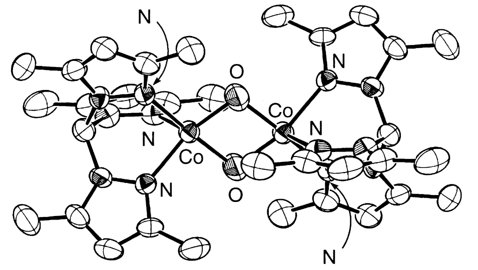
The thermal stability of $\mathbf{3^{Co}}$ and $\mathbf{3^{Ni}}$ was found to be dependent on the substituent R^3 proximal to the metal center. The isopropyl derivatives $\mathbf{3a^{Co}}$ and $\mathbf{3a^{Ni}}$ studied first were too unstable even at −78 °C to be characterized satisfactorily but later study employing the methyl-substituted ligands ($Tp^{Me_2,X}$) revealed that the obtained products were not the μ-$\eta^2:\eta^2$-O_2 species **1** analogous to the copper complex $\mathbf{1^{Cu}}$ [20] but a new type of "dioxygen complex", i.e. higher-valent dinuclear bis(μ-oxo) complexes **3** resulting from O–O bond cleavage.[17] The unstable isopropyl derivatives $\mathbf{3a^{Co}}$ and $\mathbf{3a^{Ni}}$, however, provided us with useful information on the reactivity of the $M_2(\mu\text{-}O)_2$ core by analyzing their decomposition products.[21]

The new "dioxygen species" have been characterized by various spectroscopic methods as described below and definite structural evidence has been obtained by X-ray crystallography of the Tp^{Me_3} ($\mathbf{3b^{Co}}$ and $\mathbf{3b^{Ni}}$) and Tp^{Me_2} complexes ($\mathbf{3c^{Co}}$) (Fig. 1). Each metal center adopts square-pyramidal geometry with one of the pyrazolyl groups occupying the axial position. The most significant structural feature is the O···O separations [2.32 Å ($\mathbf{3b^{Ni}}$), 2.33 Å ($\mathbf{3b^{Co}}$), 2.27 Å ($\mathbf{3c^{Co}}$)] which exceed the distance of bonding interaction (cf. O–O single bond length: 1.48 Å). On the basis of this feature the new complexes $\mathbf{3^{Co}}$ and $\mathbf{3^{Ni}}$ are characterized as dinuclear bis(μ-oxo) species arising from O–O bond cleavage and, accordingly, the oxidation state of the metal centers is determined to be +3, which is higher than that (+2) of the starting complex **2** and the μ-$\eta^2:\eta^2$-O_2 species **1**. When the core structure of $\mathbf{3^{Co}}$ and $\mathbf{3^{Ni}}$ is compared with that of the starting complex **2** having the same four-membered M_2O_2 cyclic linkage, shrinking of the M_2O_2 core is notable [cf. Ni–O: 1.843(5), 1.857(4) ($\mathbf{3^{Me_3}Ni}$); 1.973(2), 1.979(3) Å ($\mathbf{2^{Me_3}Ni}$)] indicating increased electrostatic interaction between the more charged components, the oxo ligand(−II) and the M(+III) center [cf. in **2**: hydroxo ligand(−I)/M(+II)]. This change is associated with the inversion of the relationship of the $M–N_{eq}$ and $M–N_{ax}$ distances ($\mathbf{3^{Ni}}$: $Ni–N_{eq} < Ni–N_{ax}$; $\mathbf{2^{Ni}}$: $Ni–N_{eq} > Ni–N_{ax}$).

Oxidative dehydrogenation of the $M_2(\mu\text{-}OH)_2$ complex **2** is an alternative formation mechanism of the $M_2(\mu\text{-}O)_2$ core but this possibility has been eliminated by the failure of formation



$3b^{Ni}$



$3c^{Co}$

Fig. 1. Molecular structures of bis(μ-oxo) complexes.

of **3** upon treatment of **2** with oxidizing agents such as O_2, MCPBA (*m*-chloroperbenzoic acid), *t*-BuOOH, and $KMnO_4$. It is therefore concluded that **3** should be formed via homolytic O–O cleavage of the μ-η^2:η^2-O_2 intermediate **1** (Scheme 3). We also examined a labeling experiment using $H_2{}^{18}O_2$ but very fast exchange of the bridging oxo ligands in **3** with external water molecules hampered definite confirmation of the O–O cleavage process.

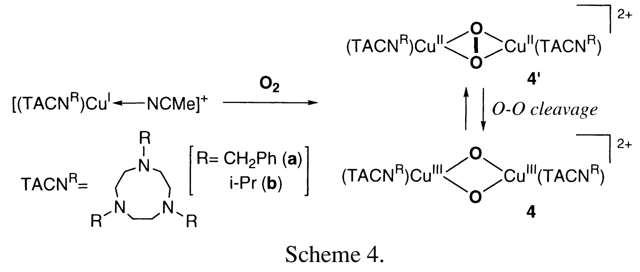
Complexes $\mathbf{3^{Co}}$ and $\mathbf{3^{Ni}}$ were the first examples of dinuclear higher-valent bis(μ-oxo) species of cobalt and nickel, which were followed by the studies of the nickel complexes by Suzuki, Itoh, and Riordan.[22] Analogous higher-valent bis(μ-oxo) species were already reported by Tolman for the copper-TACN^R systems (**4**; TACN: 1,4,7-triazacyclononane), which were obtained by O_2-oxidative addition (Scheme 4).[23] It was also revealed that, depending on the solvent, the bis(μ-oxo) (**4**) and μ-η^2:η^2-O_2 structures (**4′**) were interconverted with each other via a reversible O-O cleavage process, but such a phenomenon was not observed for the cobalt and nickel systems.

The bis(μ-oxo) complexes $\mathbf{3^{Co}}$ and $\mathbf{3^{Ni}}$ are also characterized spectroscopically. The nickel complex $\mathbf{3^{Ni}}$ shows two intense UV-vis absorptions around 300 and 400 nm (see also Fig. 2), which are similar to those of the copper complex **4** and are ascribed to O→M LMCT transitions as analyzed for a related copper system by Solomon.[24] The apparent diamagnetism of $\mathbf{3^{Ni}}$ suggested by the ^{1}H-NMR signals appearing in the normal region and the lack of ESR signal should be a result of strong antiferromagnetic coupling of the two low-spin Ni^{III} centers (d^7, S = 1/2). The ^{1}H-NMR spectrum observed at a low temperature contained only one set of the pyrazolyl signals indicating occurrence of fast exchange of the axial and equatorial pyrazolyl groups via pseudo-rotation. Because similar features have been observed for the recently reported $Ni^{III}{}_2(\mu\text{-}O)_2$ species, these features turn out to be common for the $M^{III}{}_2(\mu\text{-}O)_2$ core (M = Cu, Ni).[22,23]

The cobalt complex $\mathbf{3^{Co}}$ belongs to a rare class of five-coordinate Co^{III} species.[25] Co^{III} species usually adopt a coordinatively saturated, six-coordinate structure, which is too kinetically as well as thermodynamically inert to exhibit any notable reactivity, especially, in oxygenation reaction. In contrast to the usual diamagnetic six-coordinate Co^{III} complexes the five-coordinate coordinatively unsaturated bis(μ-oxo) complex $\mathbf{3^{Co}}$ gives an isotropically shifted ^{1}H-NMR spectrum spreading over the range between 27 to −35 ppm and a single intense UV-vis band around 350 nm. The unique spectroscopic features and remarkable reactivity of $\mathbf{3^{Co}}$ could be ascribed to the above-mentioned unusual structure; these features are also considerably different from those of the copper and nickel complexes discussed above.

These spectroscopic features can be interpreted in terms of the simplified d-electron configurations of each metal center shown in Chart 2. The strong interaction of the highly negatively charged oxo ligand(−II) with the metal d orbitals leads not only to the structural deformation ($M\text{–}N_{ax} > M\text{–}N_{eq}$) but also to the coordination environment similar to that given by a square-planar N_2O_2 donor set with a substantial energy gap between $d_{x^2\text{-}y^2}$ and the next orbital (d_{z^2} or d_{xy}). Accordingly, the five-coordinate square-pyramidal and four-coordinate square-planar bis(μ-oxo) species of copper show very similar spectroscopic features.[24] In the case of the nickel system $\mathbf{3^{Ni}}$, the large energy gap causes a low-spin electronic configuration, and antiferromagnetic spin coupling of the unpaired electrons should lead to the apparent diamagnetism, whereas the cobalt complex $\mathbf{3^{Co}}$ with the small energy gap between the d_{xy} and d_{z^2} leads to a medium spin configuration with two unpaired electrons (S = 1), which gives rise to the isotropically shifted ^{1}H-NMR spectrum.

The results hitherto described raise the question "Why do the dinuclear "dioxygen" complexes of the same composition $Tp^RM(\mu\text{-}``O_2")MTp^R$ adopt two different structures, the μ-η^2:η^2-O_2 (**1**) and bis(μ-oxo) structures (**3**), depending on the central metals?". The difference could be explained in terms of the energy levels of metal d-orbitals. The dioxygen complexes are formed by cooperative forward and backward donation between the metal centers and the O_2 ligand. A schematic presentation for the two types of back-donation from the two metal centers to the O_2 ligand in **1**-type complex is shown in Chart 3. The back-donation from the two filled metal d-orbitals to the O_2 π^*-orbital is so effective that the O–O vibration appears in the region as low as ~750 cm^{-1}, while similar interaction is also operative for mononuclear complexes to a lesser extent.[26] In addition to this type of interaction, the O_2 σ^*-orbital in **1** is arranged so as to effectively overlap with the d-or-



Scheme 4.

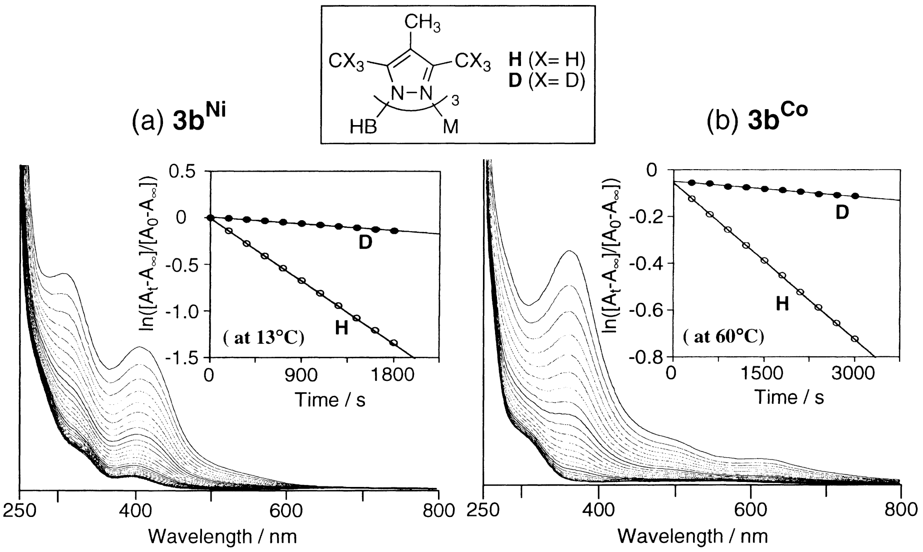


Fig. 2. Spontaneous thermal decomposition of $\mathbf{3b}^{Ni}$ and $\mathbf{3b}^{Co}$ followed by UV-vis spectroscopy.

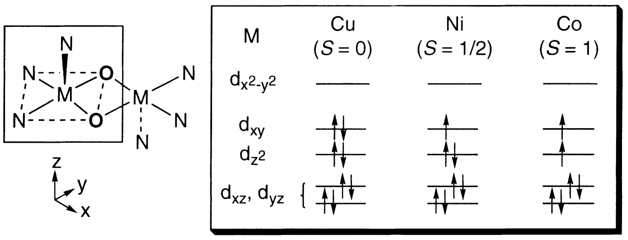


Chart 2.

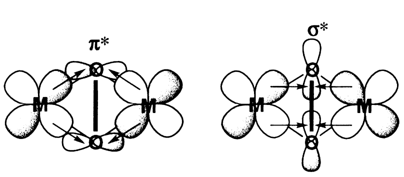


Chart 3.

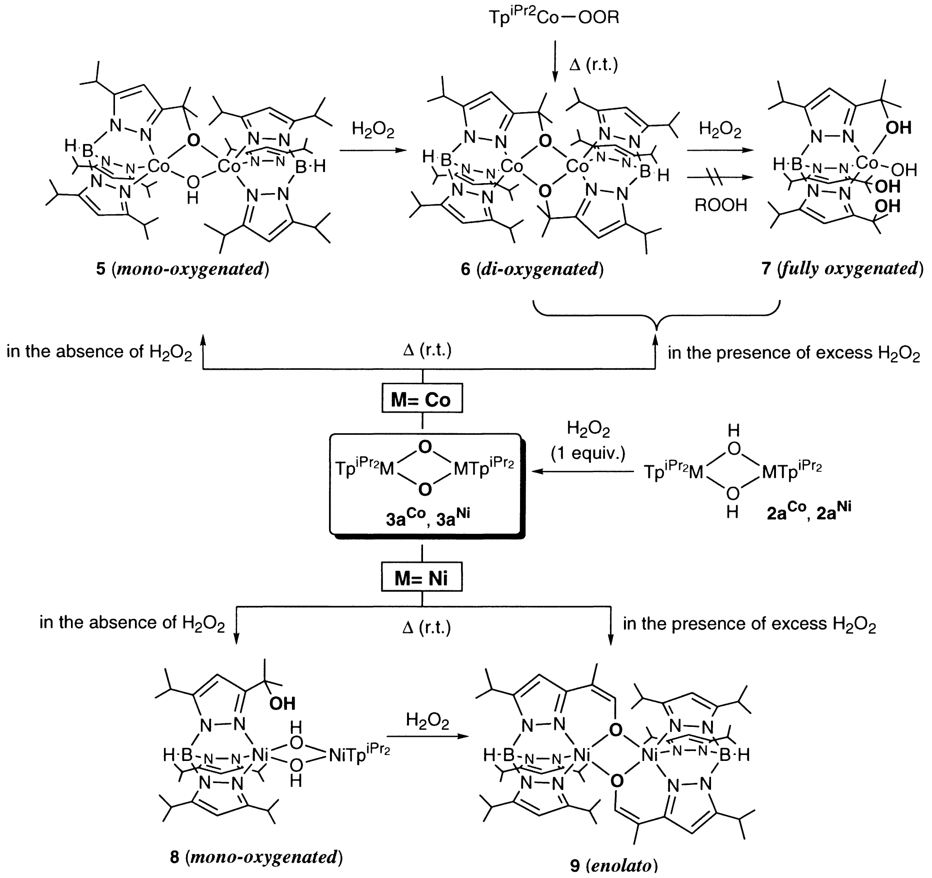
bital of different symmetry. The additional interaction should further weaken the O–O bond and may finally cleave it, if it works sufficiently. On the periodic table, the closer an element is located to the left end of the row, the higher the orbital energies become (Cu: −10.70 eV; Ni: −10.00 eV; Co: −9.00 eV; taken from CAChe ver. 4.0). The energy levels of the cobalt and nickel systems should be high enough for the effective back donation to the O_2 σ^*-orbital, which brings about the O–O bond cleavage to give the bis(μ-oxo) structure (**3**). In accord with this consideration, the copper complex coordinated by the more electron-donating sp^3-nitrogen atoms (e.g. TACN^R in **4**) undergoes O–O cleavage,[23] whereas $\mathbf{1}^{Cu}$ coordinated by the less electron-donating sp^2-nitrogen atoms retains the O–O linkage.[11]

1.1.2. Reactivity and Reaction Mechanisms.[21] The bis(μ-oxo) complexes $\mathbf{3}^{Co}$ and $\mathbf{3}^{Ni}$ were thermally unstable; through analysis of the decomposed products information concerning the reactivity of the $M_2(\mu\text{-}O)_2$ core was obtained. The isopropyl derivatives $\mathbf{3a}^{Co}$ and $\mathbf{3a}^{Ni}$ were much less stable than the methyl derivatives **3b–d** as mentioned above and underwent spontaneous decomposition even at a low temperature. The results are summarized in Scheme 5.

Thermal decomposition of the cobalt complex $\mathbf{3a}^{Co}$ afforded the red product **5**, where, of the twelve isopropyl-methine groups, one proximal to the metal center was oxidized to give the tertiary alkoxy functional group bridging the two metal centers, as determined by X-ray crystallography. When the decomposition was carried out in the presence of an excess amount of H_2O_2, two new products **6** and **7** were isolated from the reaction mixture. The blue product **6** proved to be the dinuclear species, where the alkoxy-side mononuclear structure in **5** was dimerized through the two alkoxy bridges, and thus resulted from oxygenation of two isopropyl-methine groups in $\mathbf{3a}^{Co}$. The other brown product **7** was determined to be the mononuclear species, where all the three R^3-isopropyl-methine groups were oxygenated. Let us note that treatment of isolated samples of **5** and **6** with H_2O_2 produced **6** and **7**, respectively, suggesting that the three oxygenated complexes **5**, **6** and **7** were formed by sequential oxygenation reactions of $\mathbf{3a}^{Co}$. Complex **6** was also obtained by thermolysis of the alkylperoxo complex as will be described below.[21]

The trimethyl derivative $\mathbf{3b}^{Co}$ also underwent spontaneous thermal decomposition to give the ligand-oxygenated product $\mathbf{10b}^{Co}$ (Chart 4) analogous to **5**.[17]

It is remarkable that the bis(μ-oxo) species $\mathbf{3}^{Co}$ can oxidize the hydrocarbyl moiety of the Tp^R ligand. The specific oxygenation of the isopropyl-methine moieties proximal to the metal center (R^3) in the thermolysis products verifies that the active species is generated on the metal center. It is obvious that the formation mechanism of the oxygenated products involves C–H bond cleavage and C–O bond formation processes. In addition, the instability (high reactivity) of the isopropyl complex **3a** compared to the methyl complexes **3b–d** shows that the intermediates should be radical or carbocationic species generated by H-abstraction, because such species are stabilized by more substitution (a tertiary alkyl species from the isopropyl group vs. a primary alkyl species from the methyl group).



Scheme 5.

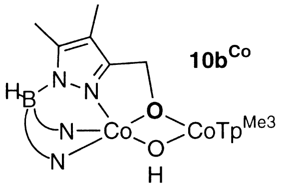
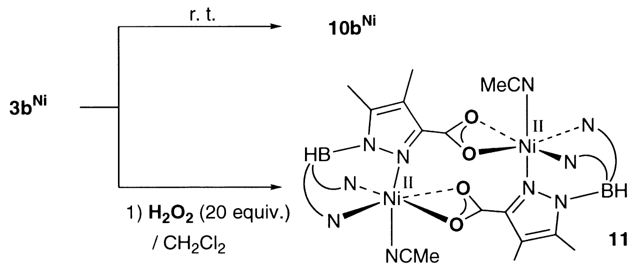


Chart 4.



Scheme 6.

Similar thermolysis processes were observed for the nickel complexes $\mathbf{3}^{\mathrm{Ni}}$. The green product **8** obtained from the isopropyl complex $\mathbf{3a}^{\mathrm{Ni}}$ was identified as the dinickel di(μ-hydroxo) complex bearing the hydroxylated substituent (R^3), which corresponded to the hydrated form of the cobalt complex **5** (Scheme 5). In this case, too, decomposition in the presence of an excess amount of H_2O_2 gave another product, the enolato complex **9** resulting from a combination of dehydrogenation and oxygenation. Thermolysis of the trimethyl complex $\mathbf{3b}^{\mathrm{Ni}}$ in the absence and presence of an excess amount of H_2O_2 afforded $\mathbf{10b}^{\mathrm{Ni}}$ (the nickel derivative of $\mathbf{10b}^{\mathrm{Co}}$) and **11**, respectively (Scheme 6).[17,27] The carboxylato complex **11** resulted from multiple oxidation of the proximal methyl group (R^3) in the $\mathrm{Tp}^{\mathrm{Me}_3}$ ligand.

In contrast to the isopropyl complexes $\mathbf{3a}^{\mathrm{Co}}$ and $\mathbf{3a}^{\mathrm{Ni}}$ which slowly decomposed even below -50 °C, the methyl complexes $\mathbf{3b–d}^{\mathrm{Co}}$ and $\mathbf{3b–d}^{\mathrm{Ni}}$ turned out to be stable enough to be handled even at ambient temperature for a moment and then were subjected to kinetic analyses of the decomposition processes, which were followed by monitoring UV-vis absorptions. Figure 2 shows changes of the UV absorptions of the trimethyl derivatives observed at 13 °C ($\mathbf{3b}^{\mathrm{Ni}}$) and 60 °C ($\mathbf{3b}^{\mathrm{Co}}$). The decay processes indicated as **H** follows first order kinetics with respect to **3** obeying the equation, $d[\mathbf{3}]/dt = -k[\mathbf{3}]$, and the activation parameters $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and Ea derived from the Eyring plots are summarized in Table 1. The kinetic parameters for $\mathbf{3b}^{\mathrm{Co}}$ and $\mathbf{3b}^{\mathrm{Ni}}$ are comparable to the related copper-TACN$^{\mathrm{R}}$ complexes **4** as shown in Table 2.

First of all, the activation enthalpy values of the nickel complexes $\mathbf{3b–d}^{\mathrm{Ni}}$ are smaller than those of the corresponding cobalt complexes $\mathbf{3b–d}^{\mathrm{Co}}$ by several kcal mol^{-1}. In fact, the decay rate of the nickel complex $\mathbf{3b}^{\mathrm{Ni}}$ is ca. 10^3 times greater than that of the Co analogue $\mathbf{3b}^{\mathrm{Co}}$ at 289 K [$\mathbf{3b}^{\mathrm{Ni}}$ (measured): 1.0×10^{-3} s^{-1}, $\mathbf{3b}^{\mathrm{Co}}$ (extrapolated using the Eyring plot): 8.0×10^{-7}

Table 1. Kinetic Parameters for the Spontaneous Thermal Decomposition Reactions of the Bis(μ-oxo) Complexes, $(\mathrm{Tp}^{\mathrm{Me_2,X}})\mathrm{M_2}(\mu\text{-O})_2$ **3b**-**d**[a)]

	k/s^{-1}	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/e.u.	Ea/kcal mol^{-1}	ln A
Nickel complexes (283 K)					
3b$^{\mathrm{Ni}}$ (X = Me)	$5.1(2) \times 10^{-4}$	18.3(1)	−8.8(5)	18.9(1)	26.0(3)
3b$^{\mathrm{Ni}}$-d_{36}	$5.6(2) \times 10^{-5}$	18.7(2)	−11.7(8)	19.3(2)	24.5(4)
3c$^{\mathrm{Ni}}$ (X = H)	$3.9(1) \times 10^{-4}$	19.0(2)	−6.8(8)	19.6(2)	27.0(4)
3d$^{\mathrm{Ni}}$ (X = Br)	$3.2(1) \times 10^{-4}$	17.6(4)	−12.1(15)	18.1(4)	24.3(8)
Cobalt complexes (333 K)					
3b$^{\mathrm{Co}}$ (X = Me)	$2.2(1) \times 10^{-4}$	24.0(3)	−3.4(9)	24.6(3)	28.9(5)
3b$^{\mathrm{Co}}$-d_{36}	$2.2(1) \times 10^{-5}$	25.7(6)	−2.7(17)	26.4(6)	29.2(9)
3c$^{\mathrm{Co}}$ (X = H)	$4.4(1) \times 10^{-4}$	21.5(3)	−9.6(10)	22.1(3)	25.7(5)
3d$^{\mathrm{Co}}$ (X = Br)	$3.1(1) \times 10^{-4}$	22.7(2)	−7.1(5)	23.3(2)	27.0(2)

a) Solvent: THF (**3b** and **3c**), toluene (**3d**). **3b**-d_{36} = $[\mathrm{Tp}^{3,5\text{-}(\mathrm{CD_3})_2,4\text{-}\mathrm{CH_3}}\mathrm{M}]_2(\mu\text{-O})_2$. **3b**$^{\mathrm{Ni}}$ and **3b**$^{\mathrm{Co}}$: the averaged value for 9 experiments; the others: the averaged value for 3 experiments.

Table 2. Comparison of the Activation Parameters for the Spontaneous Thermal Decomposition Reactions of Various Bis(μ-oxo) Complexes[a)]

	$k_{\mathrm{H}}/k_{\mathrm{D}}$(temp/K)	$\Delta\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta\Delta S^{\ddagger}$/e.u.	$A_{\mathrm{H}}/A_{\mathrm{D}}$
$[\mathrm{Tp}^{\mathrm{Me_3}}\mathrm{Ni}^{\mathrm{III}}]_2(\mu\text{-O})_2$ (**3b**$^{\mathrm{Ni}}$)	9 (1) (283)	0 (1)	−3 (1)	4.2(1)
$[\mathrm{Tp}^{\mathrm{Me_3}}\mathrm{Co}^{\mathrm{III}}]_2(\mu\text{-O})_2$ (**3b**$^{\mathrm{Co}}$)	10 (1) (343)	2 (1)	1 (2)	0.7(1)
$[\mathrm{Tp}^{i\mathrm{Pr},\mathrm{Me}}\mathrm{Co}^{\mathrm{III}}]_2(\mu\text{-O})_2$[28]	22 (1) (281)	2.5	4	0.13
$[\mathrm{TACN}^{\mathrm{Bn_3}}\mathrm{Cu}^{\mathrm{III}}]_2(\mu\text{-O})_2$ (**4a**)[b),23]	14 (1) (293)	2.5	3	0.20(5)
$[\mathrm{TACN}^{i\mathrm{Pr_3}}\mathrm{Cu}^{\mathrm{III}}]_2(\mu\text{-O})_2$ (**4b**)[b),23]	12 (1) (293)	1.8	2	0.49(5)
$[\mathrm{TACN}^{i\mathrm{Pr_3}}\mathrm{Cu}^{\mathrm{II}}]_2(\mu\text{-}\eta^2\!:\!\eta^2\text{-O}_2)$[23,29]	18 (1) (298)	~0	−4	~6

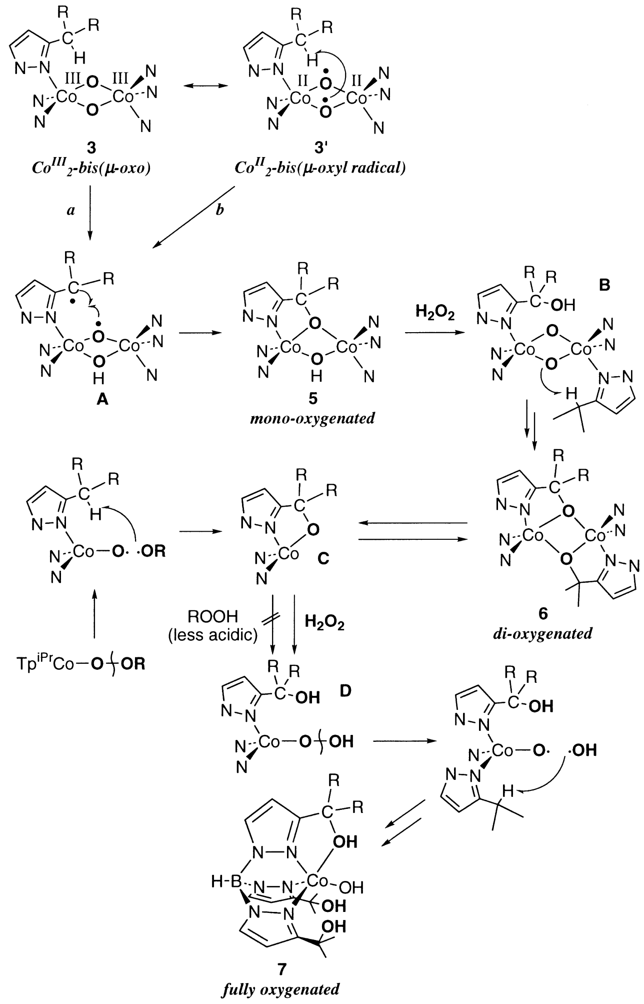
a) $\Delta\Delta H^{\ddagger} = \Delta H^{\ddagger}_{\mathrm{D}} - \Delta H^{\ddagger}_{\mathrm{H}}$; $\Delta\Delta S^{\ddagger} = \Delta S^{\ddagger}_{\mathrm{D}} - \Delta S^{\ddagger}_{\mathrm{H}}$. b) See Scheme 4.

s^{-1}]. The plots **D** in Fig. 2 are for **3b**$^{\mathbf{Co}}$-d_{36} and **3b**$^{\mathbf{Ni}}$-d_{36} in which the methyl groups at the R^3 and R^5 positions are deuterated. As is evident from the plots, the decay rate constants decrease to ca. 1/10 of those of the H-compounds **3b**$^{\mathbf{Co}}$ and **3b**$^{\mathbf{Ni}}$ clearly indicating that the H-abstraction from the methyl substituent (R^3) is the rate-determining step of the present spontaneous thermal decomposition. This result is consistent with the above-mentioned qualitative interpretation of the stability, i.e. the stability of the bis(μ-oxo) complexes **3**$^{\mathbf{Co}}$ and **3**$^{\mathbf{Ni}}$ is correlated with the stability of the radical or carbocationic species generated by H-abstraction. When the molecular structures determined by X-ray crystallography (Fig. 1) are closed up in detail, close contacts (2.18–2.68 Å) are found between the methyl hydrogen atom and the μ-oxo ligand, suggesting that the methyl hydrogen atoms could approach the reactive μ-oxo oxygen atom.

As described in the introductory part, the Tp$^{\mathrm{R}}$-substituent R^4 doesn't affect the steric coordination property but does effect the electronic property through the pyrazolyl ring's π-system. In order to examine the electronic effect of the R^4 substituent, the three derivatives **3b–d**$^{\mathbf{Co}}$ and **3b–d**$^{\mathbf{Ni}}$ containing H (Tp$^{\mathrm{Me_2}}$), the electron-releasing group (Me; Tp$^{\mathrm{Me_3}}$) and the electron-withdrawing group (Br; Tp$^{\mathrm{Me_2,Br}}$) were prepared and subjected to the kinetic analysis. Although we expected that an electron-withdrawing group should increase the electrophilicity of the μ-oxo group (k: Br > H > Me), the results were not as we expected. Furthermore, different tendencies were observed for the cobalt and nickel series [k: Me > H > Br (Ni); H > Br > Me (Co)]. The lack of apparent relationship between the decay rates and the electronic property of R^4 indicates that not only the electronic structure of the μ-oxo ligand but also the relative orientation of the methyl-hydrogen atom to be abstracted with respect to the μ-oxo ligand affects the reaction rates.

On the basis of the above-mentioned results we propose the reaction mechanisms summarized in Scheme 7 for the spontaneous thermal decomposition of the bis(μ-oxo) complexes of cobalt **3**$^{\mathbf{Co}}$.

The μ-oxo ligand in the higher-valent species **3** should be electrophilic enough to abstract a hydrogen atom at R^3 to give the diradical intermediate **A** (route a). This process can be alternatively regarded as follows. The dinuclear trivalent bis(μ-oxo) species **3** can be viewed as the dinuclear divalent bis(μ-oxyl radical) species **3′**, because the Tp$^{\mathrm{R}}$ ligand tends to stabilize lower valent species;[4] while many Tp$^{\mathrm{R}}$Co$^{\mathrm{II}}$ and several Tp$^{\mathrm{R}}$Co$^{\mathrm{I}}$ species (e.g. CO and N$_2$ complexes) are known, to the best of our knowledge only one type of Tp$^{\mathrm{R}}$Co$^{\mathrm{III}}$ complexes $[\mathrm{Tp}^{\mathrm{H}}\mathrm{Co}^{\mathrm{III}}(\kappa^3\text{-L})]^{n+}$ (κ^3-L/n = Tp$^{\mathrm{H}}$/1, diethylenetriamine/2, TACN$^{\mathrm{H3}}$/2) has been reported so far.[30] Thus electron transfer from the μ-oxo ligand to the Co$^{\mathrm{III}}$ center in **3** would give rise to the Co$^{\mathrm{II}}$ resonance contributor **3′**, the oxyl radical center in which would abstract a hydrogen atom in R^3 (route b). The radical coupling in **A** should produce the mono-oxygenated product **5** and **10b**$^{\mathbf{Co}}$. The decomposition in the absence of an excess amount of H$_2$O$_2$ is terminated at this stage. In the presence of an excess amount of H$_2$O$_2$, however, the (μ-hydroxo)-(μ-alkoxo) functional group in **5** should also be susceptible to dehydrative condensation with H$_2$O$_2$ like **2** to form the hydroxylated bis(μ-oxo) intermediate **B**. The intramolecular oxygen-

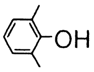
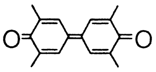
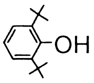
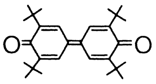


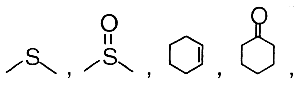
Scheme 7.

ation of **B** similar to that observed for **3** furnishes the dioxygenated product **6**. Dissociation to give **C** followed by condensation with H_2O_2 should form the hydroperoxo intermediate **D**, which causes oxygenation of the remaining R^3 group to give the fully oxygenated product **7**. This mechanism can explain the higher reactivity of the isopropyl complex **3a**^{Co} compared to the methyl complexes **3b–d**^{Co}, because the tertiary radical intermediates formed by H-abstraction from the isopropyl group (R^3) are much more stable than the primary radical species generated from the methyl substituent.

The mechanism for the initial ligand oxidation process of the nickel system should be similar to Scheme 7. As for the instability of **3**^{Ni} compared to **3**^{Co}, because (1) the d-orbital energy levels of nickel are lower than those of cobalt and (2) Ni favors the +II oxidation state more strongly than Co does (i.e. increased contribution of the Ni$^{II}_2$-bis(μ-oxyl radical) resonance form **3′**^{Ni}), the nickel center should be more electrophilic than the cobalt center. In the presence of an excess amount of H_2O_2, the ligand-oxidation pattern of the nickel system was clearly different from that observed for the Tp^{iPr_2}Co system (Scheme 7). The selective transformation of two of the six alkyl groups proximal to the metal center into the enolato groups should also be mediated by the highly reactive Ni$^{III}_2$(μ-O)$_2$ species, although details of the mechanisms have remained to be studied. Mechanisms analogous to Scheme 7 have been proposed for the related copper (**4**) and nickel systems.[31]

Table 3. Oxidation of External Substrates by the Bis(μ-oxo) Complexes **3b**^{Co} and **3b**^{Ni}

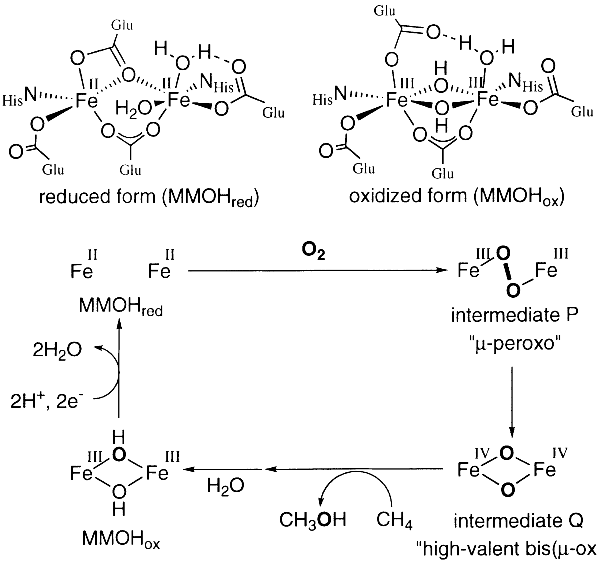
Substrate	Product	Conditions	Yields of products	
			3b^{Ni}	**3b**^{Co}
		r.t., 1 h	36	66
		r.t., 1 h	6	66
PPh_3	O=PPh_3	r.t., 48 h	0	19
CO	[Tp^{Me_3}M^{II}]$_2$(μ-CO_3)	0 °C, 1 h	0	100



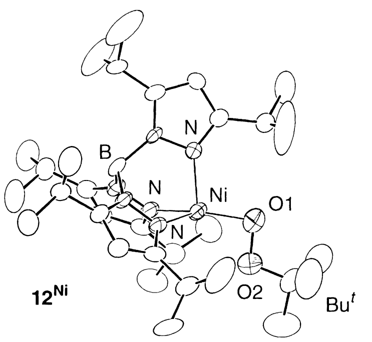
, O_2,CO_2: no reaction

We also examined oxygenation of external substrates; some typical results for **3b**^{Co} and **3b**^{Ni} are shown in Table 3. Phenols were converted to diphenoquinones via dehydrogenative dimerization, and PPh_3 and CO were oxidized to the corresponding oxides via oxo-transfer. Although the yields of the cobalt system are higher than those of the nickel system, this does not always mean that the cobalt complex **3b**^{Co} is more reactive than the nickel complex **3b**^{Ni}. For the nickel complex **3b**^{Ni} undergoes the rapid spontaneous decomposition even in the absence of a substrate. The present oxo transfer reaction is remarkable, because most reactions of the related bis(μ-oxo) species reported by other researchers are initiated by H-abstraction as in the formation of diphenoquinone.[31]

Through an extension of the bioinorganic study of the Tp^{R}M-O_2 system to some metal systems which are irrelevant to biological systems we have had an opportunity to tackle a new activated form of dioxygen species, dinuclear higher-valent bis(μ-oxo) complexes **3**^{Co} and **3**^{Ni}. Recently, this type of species has been proposed as the key intermediate in the O_2-activation by *methane monooxygenase*, which catalyzes selective conversion of methane (an extremely inactive hydrocarbon) into methanol at ambient temperature and pressure. O_2 molecule is usually incorporated into metalloprotein as a peroxide (O_2^{2-}). Such fixation is essential to pick up gaseous O_2 molecules present at a low concentration into the coordination sphere of the active site in metalloprotein. But from the viewpoint of oxygenation such reductive activation of O_2 is not favorable, because "oxygenation" is a process, where electron(s) in a substrate is transferred to the catalytic species or oxidizing agent. In order to perform an effective oxygenation reaction, therefore, it is crucial to convert the reductively activated, electron-rich O_2^{2-} species into an electrophilic species, which is reactive enough to interact with electrons in a substrate. The conversion of the μ-η^2:η^2-peroxo species into the higher-valent bis(μ-oxo) species via O–O bond cleavage (intermediate P → Q) is now recognized as one plausible O_2 activation mechanism operating for *methane monooxygenase* (Scheme 8).[32] It should be noted that this proposal does not result from the studies of metalloproteins but from the bioinorganic studies[33] including our Tp^{R}M system. Hence the bioinorganic studies



Scheme 8.



12^{Ni}

12^a	M	R	R'	M-O1	O1-O2	< M-O1-O2
12^{Mn}	Mn	Bu^t,Pr^i	CMe_2Ph	1.964(3)	1.411(4)	105.1(2)
12^{Co}	Co	Bu^t,Pr^i	CMe_2Ph	1.88(1)	1.36(1)	116.7(8)
12^{Ni}	Ni	Pr^i_2	Bu^t	1.853(7)	1.440(7)	96.2(4)
12^{Cu}	Cu	Pr^i_2	CMe_2Ph	1.916(4)	1.460(4)	112.1(4)
$12^{Pd\ b}$	Pd	Pr^i_2	Bu^t	1.981(4)	1.440(5)	114.2(3)

[a] Tp^RM-OOR'; bond lengths in Å and bond angles in deg.
[b] $Tp^{iPr2}(py)Pd$-$OOBu^t$ (see section 2.1).

Fig. 3. Structures of Tp^RM-OOR′ complexes **12**.

using well-characterized low-molecular weight complexes turn out to serve as very powerful tools for elucidation of reaction mechanisms of biological processes.

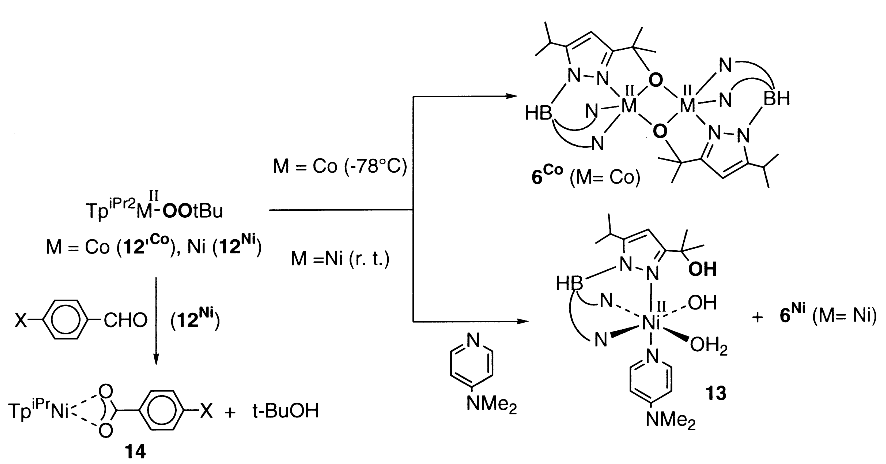
1.2. Alkylperoxo Complexes.[34] Together with the metal-O_2 adducts discussed above, alkylperoxometal species (M-OOR′) have been regarded as key intermediates of metal-catalyzed autoxidation reactions and oxygenation reactions using R′OOH as the stoichiometric oxidant[35] (e.g. Sharpless asymmetric oxidation)[36] and a considerable number of reports on isolation and characterization of M-OOR′ species have appeared.[37] But the previous studies have focused on the early transition metal complexes (e.g. V, Ti), the Fe^{III} species studied as models for non-heme iron enzymes, and the Co^{III} species related to autoxidation and the stable group 10 metal complexes (Pt). No systematic study using a common ligand system has been reported so far and little is known about the chemistry of alkylperoxo complexes of lower valent metals.

The "dehydrative condensation" with the hydroxo complexes **2** is effective for the synthesis of not only the "dioxygen" complexes described above but also a series of alkylperoxo complexes, Tp^RM-OOR′ **12** (M = Mn, Co, Ni, Cu, Pd) (Scheme 2). For the manganese and cobalt complexes, kinetic stabilization by the bulky $Tp^{tBu,iPr}$ ligand was essential for their isolation[34a,d] and an analogous reaction of the iron complex $\mathbf{2^{Fe}}$ resulted in condensation as well as oxidation of the metal center to give $[Tp^{tBu,iPr}Fe^{III}\text{-}OOBu^t]^+$ $\mathbf{12'^{Fe}}$ characterized by a combination of resonance Raman, UV-vis and ESR spectroscopy.[34b] The palladium complex **16** will be discussed in the next section. The isolated alkylperoxo complexes **12** have been characterized by crystallographic and spectroscopic methods; the molecular structure of the nickel complex $\mathbf{12^{Ni}}$ [34c] and the structural parameters associated with the M-OOR moiety are shown in Fig. 3. The M–O and O–O lengths fall in the typical ranges of the single bond lengths but significant bending of the M–O–O linkage is noted for $\mathbf{12^{Ni}}$ and $\mathbf{12^{Mn}}$ (when the bulkiness of the $Tp^{tBu,iPr}$ ligand is taken into account), while the angles for the other complexes are comparable to that for an sp^3-hybridized atom. The bending is associated with the distortion of the coordination geometry from a tetrahedral C_{3v} structure to a trigonal-bipyramidal C_s structure resulting from weak interaction of the distal oxygen atom (O2) with the coordinatively unsaturated metal center.

Interestingly, the relative stability of the Ni and Co alkylperoxo complexes $\mathbf{12^{Co}}$ and $\mathbf{12^{Ni}}$ is reversed when compared with the bis(*μ*-oxo) complexes $\mathbf{3^{Co}}$ and $\mathbf{3^{Ni}}$. The reactive (unstable) cobalt complex bearing the Tp^{iPr_2} ligand $\mathbf{12'^{Co}}$ decomposed even at −78 °C to give the dinuclear complex $\mathbf{6^{Co}}$, the same product that had been obtained from **3** in the presence of an excess amount of H_2O_2 (Schemes 5 and 9). On the other hand, thermal decomposition of the nickel complex $\mathbf{12^{Ni}}$ proceeded over the course of 1 day at ambient temperature and oxygenation occurring at the isopropyl-methine moiety was confirmed after conversion to the dimethylaminopyridine adduct **13**.[34c] Preliminary experiments revealed that reaction of the nickel complex **13** with benzaldehyde derivatives afforded the corresponding benzoato complexes **14** and the dependence of the oxidation reaction rates on the *p*-substituents of Ar-CHO suggested that the OOR moiety showed a nucleophilic character like that found in early transition metal complexes.[37]

Thus the alkylperoxo-cobalt and -nickel complexes $\mathbf{12^{Co}}$ and $\mathbf{12^{Ni}}$ exhibit the unique oxygenation activity toward an aliphatic C–H bond. The reaction mechanism should involve radical intermediates but the reaction features are considerably different from those of the conventional free radical mechanisms (e.g. Haber–Weiss mechanism), in which transition metal ions mainly control generation of free radical intermediates (e.g. •OH, •OOH) and termination of radical processes. The results of the present study, though not completed yet, reveal that the reactivity of the L_nM-OOR species can be controlled by an appropriate combination of M and L and can contribute to development of novel oxygenation reactions involving M-OOR intermediates.

Some other mononuclear Tp^R complexes relevant to catechol dioxygenase (Fe),[38] *α*-keto acid dependent enzyme (Fe),[39] haloperoxidase(V)[40] and manganese enzymes[41] were also stud-



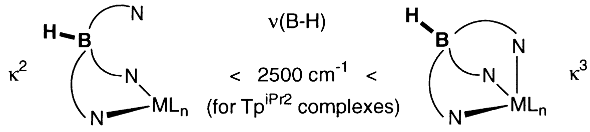
Scheme 9.

ied.

2. Second Row Transition Metal Dioxygen Complexes

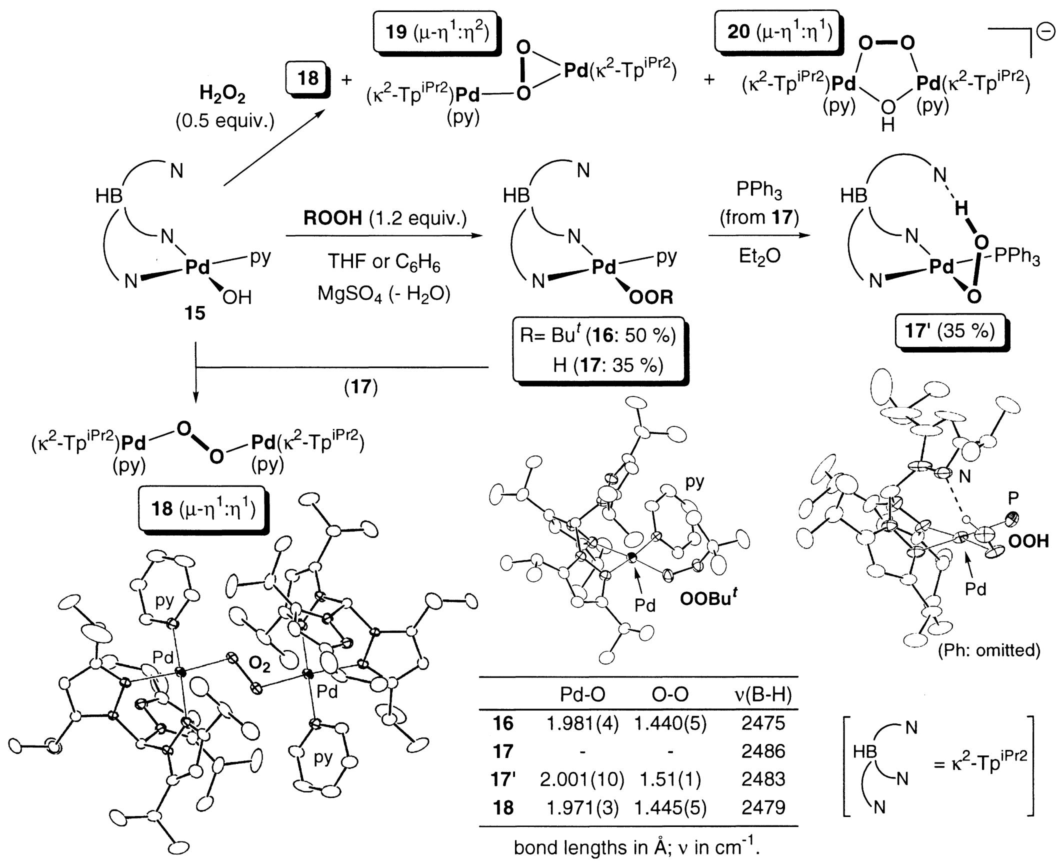
In order to obtain more detailed insight into the structure and reactivity of the transition metal-O_2 adducts, a comparative study of second row transition metal complexes has been carried out. In contrast to the rather unstable first row transition metal complexes described above, the second row transition metal complexes prove to be so thermally stable as to provide valuable information concerning the structural aspects of active dioxygen species.

Before discussion of the result for the second row transition metal complexes let us consider the coordination behavior of the Tp^R ligand. Because the Tp^R ligand has been mainly used to create a κ^3-coordination environment as described in the introductory part, little attention has been paid to the κ^2-coordination mode, which plays pivotal roles in the chemistry of d^8 metal complexes, in particular, second row transition metal complexes (e.g. Pd^{II} and Rh^{I}). In the case of the $Tp^RM(X)(Y)$-type d^8 metal complexes, the Tp^R ligand is coordinated to the metal center either in a κ^2- or κ^3-fashion to give 16e or 18e species, respectively. Such κ^3-coordination is found for Lewis acidic metal species with electron-withdrawing ligands (e.g. O-ligand) but steric repulsion also causes the hapticity change. The two rhodium-diene complexes $Tp^{iPr_2}Rh$(diene) [diene = 1,5-cyclooctadiene (cod), norbornadiene (nbd)] studied in our laboratory can be raised as typical examples.[42] While the cod complex adopts the square-planar (spl) geometry, the nbd complex comprises a mixture of the spl and trigonal-bipyramidal (tbp) species with the κ^2- and κ^3-Tp^{iPr_2} ligand, respectively, both in solution and solid as verified by spectroscopic study combined with X-ray crystallography. The difference of the structures has been attributed to the bite angle of the diene ligand. The bite angle of the cod ligand may be too large to span the axial and equatorial sites in a tbp structure. Let us point out that discrimination of the hapticity of the Tp^R ligand (κ^2 vs κ^3) in $Tp^RM(X)(Y)$-type d^8 metal complexes by NMR is not always facile, because the two structures frequently interconvert with each other at a rate faster than the NMR-coalescence time scale and the slow exchange limit can not be always attained even at low temperatures. In addition, direct information concerning the presence/absence of coordination of the pendant pz^R group can not be obtained by the conventional ^1H and ^{13}C NMR. On the basis of the results of the rhodium-diene complexes we reveal that the B–H vibration of the Tp^R ligand (2400–2600 cm^{-1}), which does not overlap with vibrations of organic functional groups, is a good indicator of its hapticity. In the case of $Tp^{iPr_2}M$ complexes, the $\nu_{B\text{-}H}$ vibration of a κ^2-coordinated ligand appears below 2500 cm^{-1}, whereas that of a κ^3-coordinated ligand appears above 2500 cm^{-1} (Scheme 10). This method is very convenient compared to X-ray crystallography and NMR spectroscopy and is complementary to these methods. Recently it was reported that ^{11}B- and ^{15}N-NMR were also useful tools for discrimination of the Tp^R-hapticity.[43]



Scheme 10.

2.1. Palladium System: Formation of a Variety of Dioxygen Complexes.[44] The first attempt that we made was synthesis of $Tp^RPd(\mu$-"O_2"$)PdTp^R$ analogous to **1** and **3** by the dehydrative condensation. The dinuclear di(μ-hydroxo) complex $\mathbf{2^{Pd}}$ was obtained but it apparently did not undergo the condensation with H_2O_2, although condensation with more acidic substrates such as acetic acid was observed.[44c] Because Pd^{II} is a typical d^8 species, in the next attempt another ancillary ligand (py) was introduced to form a square-planar species. As a result, (κ^2-Tp^R)(py)Pd-OH **15** turned out to be a versatile precursor for peroxo complexes (Scheme 11). Dehydrative condensation between **15** and ROOH afforded the corresponding *t*-butylperoxo complex (**16**) and hydroperoxo complex (**17**),[44a] and the latter was further converted to the PPh_3 derivative **17′** by ligand replacement with PPh_3.[44b] Both of the complexes were spl complexes with the κ^2-Tp^{iPr_2} ligand as revealed by NMR (non-fluxional), IR ($\nu_{B\text{-}H}$) and X-ray crystallography (for **16** and **17′**). Further dehydrative condensation of the hydroperoxo complex **17** with **15** afforded the dipalladium μ-$\eta^1:\eta^1$-peroxo complex **18** in a selective manner, while the direct 2:1 condensation between **15** and H_2O_2 gave a mixture of products, from which **18**, the μ-$\eta^1:\eta^2$-peroxo complex **19**[45] and the zwitterionic cyclic μ-$\eta^1:\eta^1$-peroxo complex **20**[45] were isolated and



	Pd-O	O-O	ν(B-H)
16	1.981(4)	1.440(5)	2475
17	-	-	2486
17'	2.001(10)	1.51(1)	2483
18	1.971(3)	1.445(5)	2479

bond lengths in Å; ν in cm^{-1}.

Scheme 11.

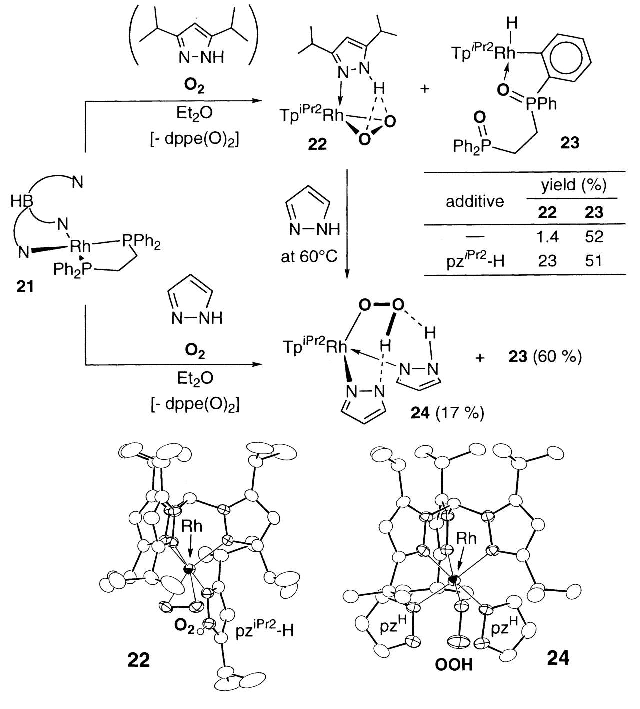
characterized by X-ray crystallography.[46] The O–O lengths of **16**–**20** fall in the range of O–O single bonds indicating that they are peroxo complexes. The Tp^{iPr_2}(py)Pd moieties in **16**–**18** adopt a typical spl geometry with the non-coordinated pendant pz^R group. It is notable that **17′** belongs to a rare class of structurally characterized hydroperoxo complexes and contains hydrogen-bonding interaction between the OOH hydrogen atom and the nitrogen atom of the pendant uncoordinated pz^R group. Such a hydrogen-bonding interaction is a common structural feature of structurally characterized MOOH species as will be discussed in the next section. The palladium complexes are stable even at ambient temperature and their oxidizing ability was sluggish as typically exemplified by the interaction of **17** with PPh_3 (for 2–3 hrs at r. t.), which resulted in the ligand replacement in preference to oxidation of the PPh_3 ligand. Only a small amount of the oxidized product ($O{=}PPh_3$) was formed, when the reaction was carried out at 0 °C. The peroxo ligand was essentially nucleophilic, because it formed a cyclic adduct with, for example, acetonitrile.[47] But it was also shown that the peroxo complexes converted vinyl ether ($CH_2{=}CHOR$) into acetate ester (CH_3COOR), although the reaction mechanism is not clear.[44a]

The study of the Tp^{R}Pd(L)-O_2 adducts reveals (1) the effectiveness of dehydrative condensation for the synthesis of dioxygen complexes and (2) a variety of O_2-coordination modes (μ-η^1:η^1, μ-η^1:η^2, and cyclic μ-η^1:η^1). In addition, (3) a series of M-OOR species including the rare hydroperoxo complex **17′** has been isolated and fully characterized.

2.2. Rhodium System: Conversion of Molecular Oxygen into a Hydroperoxo Species.[48]

Despite many attempts a Tp^{R}Rh^{III}-hydroxo complex could not be obtained. We thus examined O_2-oxidative addition to a Rh^I species. Of several Tp^{iPr_2}Rh^I(L_2) complexes [L_2 = cod, nbd, $(CO)_2$, $Ph_2P(CH_2)_nPPh_2$ (n = 1–3), Ph_2P–CH=CH–PPh_2] prepared in our laboratory,[49] only diphosphine complexes reacted with O_2 and the others remained unaffected.

Oxygenation of the 1,2-bis(diphenylphosphino)ethane (dppe) complex **21** afforded a mixture of products accompanying precipitation of dppe-dioxide, $Ph_2P({=}O)CH_2CH_2P({=}O)Ph_2$. Two products **22** and **23** were isolated after silica gel chromatographic separation (Scheme 12). As for the minor product **22**, its ^{1}H NMR spectrum reveals inclusion of a 3,5-diisopropylpyrazole (pz^{iPr_2}-H) molecule, and coordination of an O_2 molecule is suggested by the O–O vibration at 848 cm^{-1} (IR) and by the FD-MS data (m/z = 752: **21** + O_2 + pz^{iPr_2}-H − dppe). X-ray crystallography of **22** confirms that it is a six-coordinate Rh^{III} side-on (η^2) peroxo complex containing the κ^3-Tp^{iPr_2} ($\nu_{B\text{-}H}$ = 2540 cm^{-1}) and additional pz^{iPr_2}-H ligands. The Rh-O_2 moiety is typical for a Rh^{III}-peroxo complex, if one judges from the O–O [1.467(5) Å] and Rh–O lengths [2.001(4), 2.013(3) Å]. The N41···O_2 distances [2.681(6), 2.733(6) Å] and the orientation of the additional pz^{iPr_2} ring suggest the presence of hydrogen-bonding interactions, which is also supported by the spectroscopic data, i.e. the deshielded NH signal (δ_H 12.42) and the obscured N–H vibration. The hydrogen-bonding interaction verifies the nucleophilic (basic)



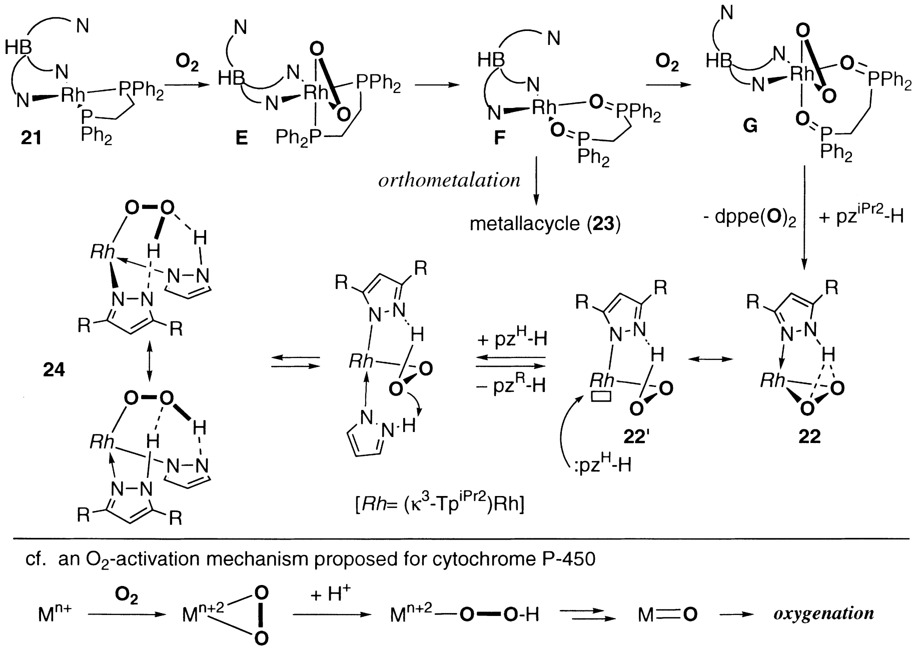
additive	yield (%)	
	22	23
—	1.4	52
pz^{iPr2}-H	23	51

Scheme 12.

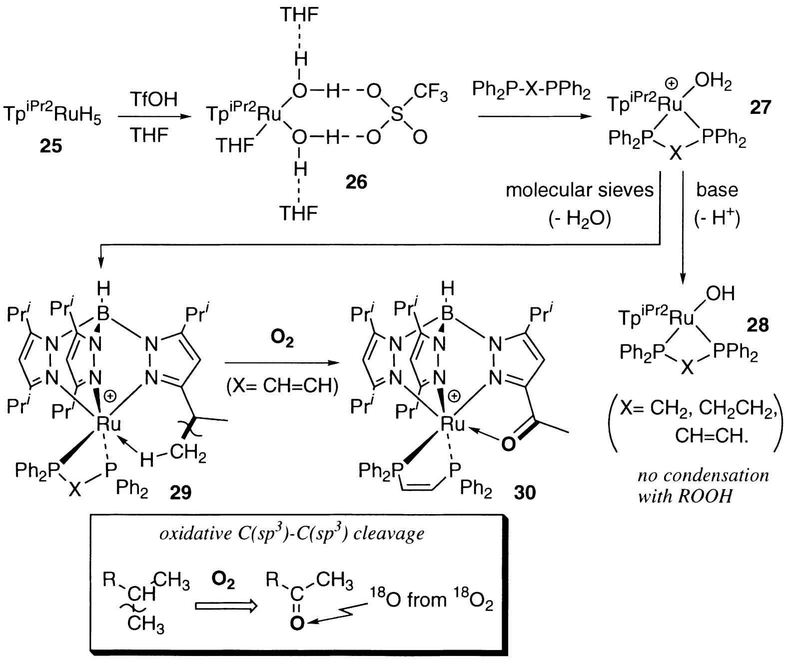
character of the peroxide ligand. Oxygenation of **21** in the presence of an equimolar amount of pz^{iPr_2}-H improved the yield of **22** to 23%. The other product **23** is a metallacyclic complex resulting from orthometalation of dppe-dioxide, as characterized by IR (ν_{BH}: 2534; ν_{RhH}: 2082 cm^{-1}), NMR [δ_H(RhH) -16.86 (d, $J = 17.5$ Hz); δ_P 57.5, 31.8 (d × 2, $J = 48$ Hz)] and X-ray crystallography. The structure of **23** indicates that **22** and **23** should be formed via oxidative addition of O_2 and the ortho C–H bond in dppe-dioxide, respectively, to the common Rh^I precursor, Tp^{iPr_2}Rh^I(dppe-dioxide) (See structure **F** in Scheme 13).

In order to examine the effect of the added pyrazole the oxygenation was carried out in the presence of the non-substituted pyrazole (pz^H-H). The yellow product **24** obtained together with **23** is suggested by the result of its FD-MS [m/z = 736: Tp^{iPr_2}Rh(O_2)(pz^H-H)$_2$] to be a η^2-peroxo complex coordinated by two molecules of pz^H-H, but X-ray crystallography reveals that it is a hydroperoxo complex formulated as Tp^{iPr_2}Rh(η^1-OOH)(pz^H)(pz^H-H), where the β-oxygen atom and the non-coordinated nitrogen atoms of the pz^H rings are held together by a hydrogen-bonding network. The O–O [1.413(8) Å] and Rh–O lengths [1.994(4) Å] are comparable to those found in **22**, and the hydrogen bonding interaction is evidenced by the N···O separation (2.78–2.85 Å), the orientation of the pz rings and the broad ^{1}H NMR signal at δ 12.03 (2H). To the best of our knowledge, only eight examples of structurally characterized hydroperoxo complexes have been reported so far.[50] (Two of them were reported by us; **17′** and **24**.) Furthermore hydrogen bonding interaction at the α- or β-oxygen atom supporting the hydroperoxo ligand is found as a common structural feature and, actually, five examples contain such an interaction. Surprisingly, the hydrogen bonding interaction in **22** and **24** makes them robust enough to survive chromatographic separation. Although hydroperoxo species have been recognized as key intermediates of biological transformations,[51] little information on their chemical properties, in particular, structural information, has been accumulated due to their extreme thermal instability.

Plausible reaction mechanisms of the rhodium system are summarized in Scheme 13. Initial O_2-oxidative addition to **21** should give the Rh^{III}(η^2-peroxo) species **E**, which is reduced to the Rh^I(dppe-dioxide) complex **F** via intramolecular O-transfer. Orthometalation of the dppe-dioxide ligand furnishes **23**,



Scheme 13.



Scheme 14.

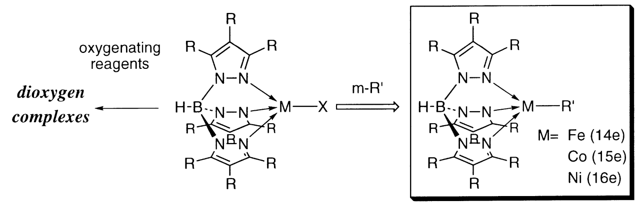
whereas the η^2-peroxo complex **22** is formed via further O_2-oxidative addition (**G**) associated with dissociation of dppe-dioxide and coordination of a pz^{iPr_2}-H molecule, which should be formed by partial decomposition of a Tp^{iPr_2}Rh species. The reaction in the presence of a bulky pz^{R}-H such as pz^{iPr_2}-H is terminated at this stage. For **22** an alternative canonical structure **22′** with a vacant coordination site can be depicted. A small pz^{R}-H molecule such as pz-H can be coordinated to the vacant site in **22′** and subsequent reorganization of the hydrogen bonding interaction affords the hydroperoxo complex **24**. The hydrogen atom of the second pyrazole is transferred to the O_2 ligand as a proton to furnish the hydroperoxo species.

Let us point out that, in the present system, an O_2 molecule is converted to a hydroperoxometal species via protonation of a cyclic η^2-peroxometal intermediate.[52] A similar process is proposed for the O_2-activation process of *cytochrome P-450* containing the heme center (Scheme 13)[53,52c–g] but the process has been supported only by spectroscopic characterization of the proposed intermediates. The present system thus provides structural evidence for the well-documented O_2-activation process and hydrogen bonding interaction plays key roles in the formation and stabilization of the activated dioxygen species.

2.3. Ruthenium System: Oxidative C–C Bond Cleavage.[54] Ruthenium is rather flexible with respect to the redox properties, and one electron redox process of Ru(II) species is expected to form a dioxygen species different from peroxide. In contrast to the rich chemistry of the Tp^{H}Ru and Tp^{Me_2}Ru systems, the chemistry of the Tp^{R}Ru system with bulky R groups has been extremely limited and we met difficulty even in the synthesis of starting compounds. After some struggle we succeeded in synthesis of the versatile, labile aquo complex **26**; obtained by protonolysis of the pentahydride complex, Tp^{iPr_2}RuH$_5$ **25** (Scheme 14).[55] Although a series of diphosphine-hydroxo complexes **28**[56] was obtained by treatment of **26** with diphosphine followed by deprotonation of the resultant aquo complex **27**, the neutral octahedral species **28** was kinetically inert and no condensation was observed with ROOH. The aquo ligand in **27**, however, was so labile as to be converted, via dehydration, to the coordinatively unsaturated species **29** stabilized by the agostic interaction with one of the C–H bonds of the isopropyl-methyl groups.[57] Complex **29** was characterized spectroscopically and crystallographically. Interaction of **29** with O_2 (in MeOH) did not result in oxidative addition as observed for the η^5-C_5R_5-derivatives, $[(\eta^5\text{-}C_5R_5)\text{Ru(diphosphine)}(OH_2)]^+$,[58] but oxygenation, the pattern of which depended on the diphosphine ligand.[54,59] The dppene complex **29** (X: CH=CH) underwent oxidative C–C bond cleavage of the isopropyl group close to the metal center to give the ketone complex **30**. The ketone oxygen atom originated from an O_2 molecule as confirmed by the labeling study using $^{18}O_2$ but the reaction mechanism presumably involving a superoxo intermediate (Ru^{III}-O_2^-) has remained to be studied. Oxygenation of the corresponding dppm and dppe complexes resulted in P-oxygenation to give a phosphine oxide coordinated complex, $[Tp^{iPr_2}Ru^{III}(Ph_2PCH_2P(=O)Ph_2)(OMe)]^+$, and oxidation of the Ru center to give a hydroxo-Ru^{III} species, $[Tp^{iPr_2}Ru^{III}(Ph_2PCH_2CH_2PPh_2)(OH)]^+$, respectively. It is remarkable that simple exposure of the Ru^{II} species **29** to O_2 produces a highly active oxidizing species that can cleave a C–C bond.

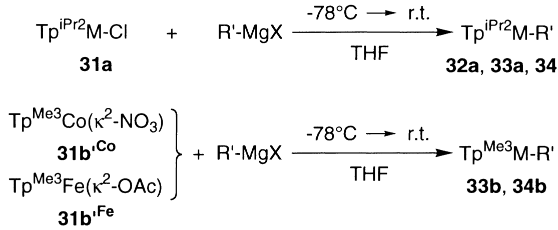
3. Organometallic Systems[2]

3.1. Highly Coordinatively Unsaturated Hydrocarbyl Complex.[60] The intriguing property of the Tp^{R} ligand as a "tetrahedral enforcer" for first row transition metal complexes prompted us to introduce a hydrocarbyl group (R′) as the σ-ligand, because the resulting complex Tp^{R}M-R′ is highly coordinatively unsaturated organometallic species with 14 (Fe), 15 (Co) and 16 (Ni) valence electrons, which are quite short of valence electrons compared to the coordinatively saturated elec-



Scheme 15.

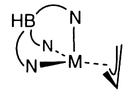
tronic configuration (18e) (Scheme 15). Coordinatively unsaturated species have been recognized as key intermediates of stoichiometric and catalytic transformations mediated by organometallic species but their chemistry has remained far less developed, because very few thermally stable species have been isolated so far.[61] It should also be noted that most of the previous coordinatively unsaturated species are kinetically stabilized by bulky hydrocarbyl groups or ancillary ligands to prevent decomposition processes such as β-hydrogen elimination reaction.[62] If the $\mathrm{Tp^R}$ ligand works as a tetrahedral enforcer for $\mathrm{Tp^RM\text{-}R'}$-type organometallic systems, we could have an opportunity to study the chemistry of *highly coordinatively unsaturated hydrocarbyl complexes which are not stabilized kinetically.*



$$\mathrm{Tp^{iPr2}M\text{-}Cl}\ (\mathbf{31a}) + \mathrm{R'\text{-}MgX} \xrightarrow[\mathrm{THF}]{-78\,^\circ\mathrm{C} \rightarrow \mathrm{r.t.}} \mathrm{Tp^{iPr2}M\text{-}R'}\ (\mathbf{32a}, \mathbf{33a}, \mathbf{34a})$$

$$\left.\begin{array}{l}\mathrm{Tp^{Me3}Co(\kappa^2\text{-}NO_3)}\ (\mathbf{31b'^{Co}}) \\ \mathrm{Tp^{Me3}Fe(\kappa^2\text{-}OAc)}\ (\mathbf{31b'^{Fe}})\end{array}\right\} + \mathrm{R'\text{-}MgX} \xrightarrow[\mathrm{THF}]{-78\,^\circ\mathrm{C} \rightarrow \mathrm{r.t.}} \mathrm{Tp^{Me3}M\text{-}R'}\ (\mathbf{33b}, \mathbf{34b})$$

	$\mathrm{Tp^R}$	M	R'	Yield (%)
$\mathbf{32a^{Fe}}$	$\mathrm{Tp^{iPr2}}$	Fe	allyl	62 (η^1)
$\mathbf{32a^{Co}}$	$\mathrm{Tp^{iPr2}}$	Co		68 (η^3) [a]
$\mathbf{32a^{Ni}}$	$\mathrm{Tp^{iPr2}}$	Ni		76 (η^3) [a]
$\mathbf{33a^{Fe}}$	$\mathrm{Tp^{iPr2}}$	Fe	*p*-methylbenzyl (η^1)	68
$\mathbf{33a^{Co}}$	$\mathrm{Tp^{iPr2}}$	Co		65
$\mathbf{33a^{Ni}}$	$\mathrm{Tp^{iPr2}}$	Ni		0
$\mathbf{33b^{Fe}}$	$\mathrm{Tp^{Me3}}$	Fe		[b]
$\mathbf{33b^{Co}}$	$\mathrm{Tp^{Me3}}$	Co		65
$\mathbf{34a^{Fe}}$	$\mathrm{Tp^{iPr2}}$	Fe	ethyl (η^1)	79
$\mathbf{34a^{Co}}$	$\mathrm{Tp^{iPr2}}$	Co		84
$\mathbf{34a^{Ni}}$	$\mathrm{Tp^{iPr2}}$	Ni		0
$\mathbf{34b^{Co}}$	$\mathrm{Tp^{Me3}}$	Co		[b]

[a]


[b] Not isolated in a pure form. See text.

Scheme 16.

$\mathrm{M^{2+}}$	Fe (d^6)	Co (d^7)	Ni (d^8)
η^1	$\boxed{\text{14e}}$	15e	16e
η^3	16e	$\boxed{\text{17e}}$	$\boxed{\text{18e}}$

☐ : observed

Chart 5.

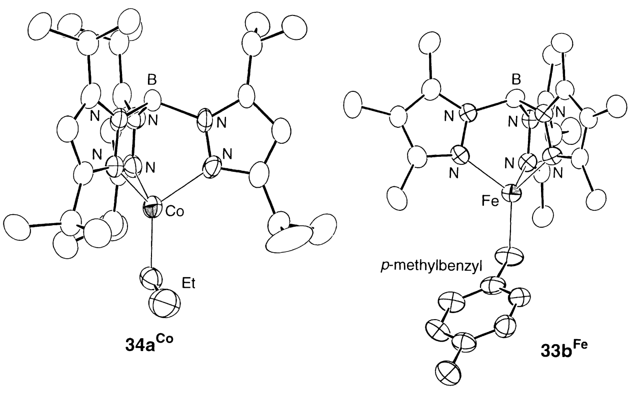


Fig. 4. Molecular structure of the alkyl complexes, $\mathbf{34a^{Co}}$ and $\mathbf{33b^{Fe}}$.

We first attempted synthesis of allyl complexes, because allyl ligand may stabilize coordinatively unsaturated metal centers through η^3-coordination.[60a,c] Treatment of the chloro complex containing the $\mathrm{Tp}^{i\mathrm{Pr}_2}$ ligand **31a** with allyl-MgCl in THF afforded yellow ($\mathbf{32a^{Fe}}$), dark orange ($\mathbf{32a^{Co}}$) and deep red products ($\mathbf{32a^{Ni}}$) in moderate yields after extraction with pentane and crystallization at a low temperature (Scheme 16). The nickel complex $\mathbf{32a^{Ni}}$ is the only diamagnetic and air- and moisture-stable species of the hydrocarbyl complexes obtained in the present study and was characterized as a η^3-allyl complex by NMR analyses. The non-substituted analogue $\mathrm{Tp^H}$-Ni(η^3-allyl) was already reported by Lehmkuhl.[63] X-ray crystallography of the three allyl complexes including paramagnetic iron and cobalt complexes $\mathbf{32a^{Fe}}$ and $\mathbf{32a^{Co}}$ verifies that the square-pyramidal cobalt and nickel complexes $\mathbf{32a^{Ni}}$ and $\mathbf{32a^{Co}}$ contain the η^3-allyl ligand, whereas the iron complex $\mathbf{32a^{Fe}}$ adopts a tetrahedral structure with the η^1-allyl ligand. We wish to point out that, although the iron atom ($\mathrm{Fe^{II}}$: d^6) contains a smaller number of d-electrons than the other two counterparts ($\mathrm{Co^{II}}$: d^7; $\mathrm{Ni^{II}}$: d^8), the resulting allyl complex $\mathbf{32a^{Fe}}$ adopts a η^1-structure with 14 valence electrons rather than a η^3-structure with 16 valence electrons closer to the coordinatively saturated electronic configuration (18e) as observed for $\mathbf{32a^{Co}}$ and $\mathbf{32a^{Ni}}$ (Chart 5). The formation of the η^1-hydrocarbyl complex $\mathbf{32a^{Fe}}$ prompted us to extend our synthetic efforts to other types of hydrocarbyl complex including benzyl (**33**) and ethyl complexes (**34**) without and with β-hydrogen atoms, respectively.[60b,c] As for the $\mathrm{Tp}^{i\mathrm{Pr}_2}$ derivatives the expected products **33a** and **34a** were obtained for the iron and cobalt systems by alkylation of the chloro complexes **31a** with appropriate Grignard reagents (Scheme 16). In the case of the less hindered $\mathrm{Tp^{Me_3}}$ derivatives, because the corresponding chloro complexes **31b** were not obtained,[8] the nitrato ($\mathbf{31'b^{Co}}$) or acetato complexes ($\mathbf{31'b^{Fe}}$) were used instead and were converted to the corresponding highly air- and moisture-sensitive alkyl complexes **33b** and **34b**, which, in a few cases, could not be obtained in analytically pure forms but could be characterized by a combination of spectroscopic analyses and chemical reactions (see below). Molecular structures of $\mathbf{33b^{Co}}$ and $\mathbf{34a^{Co}}$ are shown in Fig. 4. In contrast to the iron and cobalt complexes, a similar reaction of the nickel derivative $\mathbf{31a^{Ni}}$ resulted in decomposition to give a mixture of products, from which no characterizable component could be isolated, but carbonylation reaction confirmed formation of an analogous thermally unstable alkyl complex (see below).[64]

To our surprise the ethyl complexes **34** with 14(Fe) and 15(Co) valence electrons are very thermally stable despite the presence of β-hydrogen atoms,[61] when they are kept under an inert atmosphere. In the case of the Tp^{iPr_2} derivatives, the rather bulky isopropyl groups might contribute to kinetic stabilization of the coordinatively unsaturated species. Because, however, the thermal stability of the less hindered Tp^{Me_3} derivatives **34b** is comparable to that of the Tp^{iPr_2} derivatives **34a**, such a contribution was negligible but, as mentioned above, the former is much more sensitive to the air and moisture than the latter. Thus the stability of the Tp^RM-R′-type organometallic species should not originate from steric protection of the metal center but from their unique electronic structure, as will be discussed below.

The obtained tetrahedral alkyl complexes have been characterized by spectroscopic methods as well as by X-ray crystallography. All η^1-hydrocarbyl complexes are paramagnetic to give isotropically shifted ^{1}H NMR spectra, from which little structural information concerning the M-R moiety can be obtained.[65] One of the notable features of the η^1-alkylcobalt complexes **34**^{Co} is their blue color, which is distinct from the orange color of the η^3-allyl complex **32a**^{Co}. The different colors should be ascribed to the coordination geometry of the central metal, i.e. the tetrahedral structure of a high-spin configuration in **34**^{Co} and the square-pyramidal structure with a low-spin configuration in **32a**^{Co}. The differences are demonstrated by UV-vis spectrum and magnetic susceptibility [e.g. λ_{max}/nm (ε/cm^{-1} M^{-1}) 647 (40) (**32a**^{Co}), 388 (1030), 580 (180), 610 (210), 690 (810) (**34a**^{Co}); μ_{eff}/μ_{BM} = 1.8 (**32a**^{Co}), 4.2 (**34a**^{Co})].[66] The alkyliron complexes **32**^{Fe}, **33**^{Fe} and **34**^{Fe} are featureless compared to the cobalt complexes but their magnetic moments also reveal their high-spin configuration. The tetrahedral η^1-alkyl complexes **33** and **34** have been definitely verified by X-ray crystallography (Fig. 4). It should be noted that the core part of the ethylcobalt complex **34a**^{Co} is tetrahedral with essentially the C_3 symmetry without any additional interaction such as α- and β-agostic C–H interaction with the cobalt center, although slight distortion from a C_3-structure is observed for the benzyl-type complexes **33** as indicated by the N–M–C$_\alpha$ angles distributing in the range of 113–136° (cf. the corresponding angles for **34Co**^{iPr_2}: 123.1–125.2°). The distortion is due to a weak interaction of the electrons of the C$_\alpha$–C$_\beta$ bond with the metal center. Thus the Tp^R ligand works as a tetrahedral enforcer to give the highly coordinatively unsaturated organometallic species without kinetic stabilization. Our report has been followed by papers which described the related organometallic complexes supported by tripodal ligands **35**–**37** and similar structural features were noted (Chart 6).[67]

The chemical properties of the M–C bond in the hydrocarbyl complexes have been examined with two different aims. One is to confirm the presence of a M–C bond in the air- and moisture-sensitive hydrocarbyl complexes, single crystals of which suitable for X-ray crystallography are not always obtained, and the other is to characterize the chemical reactivity of the rare coordinatively unsaturated hydrocarbyl complexes (Scheme 17).

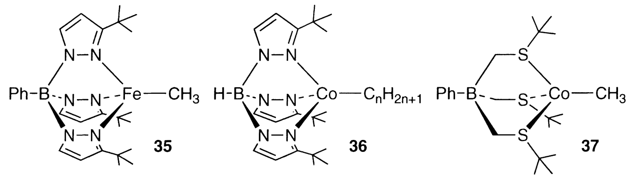
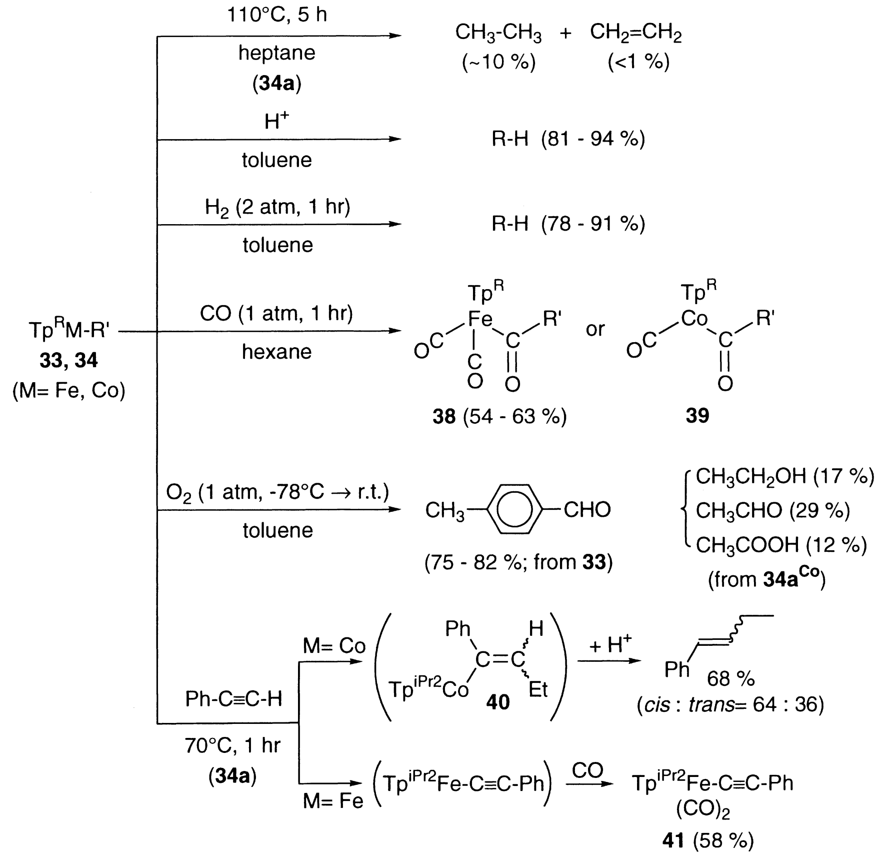


Chart 6.

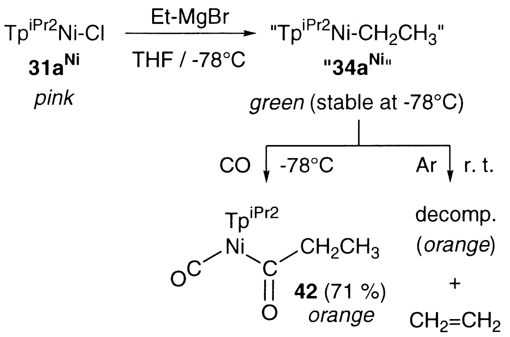
First of all, the thermal stability of the ethyl complexes **34** was examined. When heptane solutions of **34a**^{Fe} and **34a**^{Co} were heated for 5 hrs at 110 °C, formation of a trace amount (< 1%) of ethene (the product of β-hydride elimination)[61] together with a small amount (ca. 10%) of ethane (the hydrolysis product by adventitious moisture in the reaction mixture) was detected by GLC analysis of the gas phase. Similar stability was noted for **36**.[67] Monitoring the thermolysis of **34a** in toluene-d_8 by ^{1}H-NMR revealed that both of the iron and cobalt complexes were stable at 60 °C. Further heating the cobalt complex **34a**^{Co} for 11 hrs at 120 °C resulted in complete conversion into an unidentified product but, for the iron complex **34a**^{Fe}, no apparent decomposition was observed even under the same conditions. It is remarkable that despite their highly electron-deficient nature the ethyl complexes **34a** were resistant to β-hydrogen elimination, a typical thermal decomposition pathway for coordinatively unsaturated alkyl species.[61] Thermolysis of the cobalt complex **34a**^{Co} at 120 °C followed a decomposition pathway which did not produce ethene as a byproduct.

Protonolysis and hydrogenolysis of **33** and **34** afforded the corresponding alkane (R-H) in good yields and carbonylation produced carbonyl-acyl complexes **38** and **39** (Scheme 17). The diamagnetic iron complex **38**[68] was readily characterized on the basis of the IR and ^{13}C-NMR signals for the >C=O and CO functional groups. The paramagnetic cobalt complex **39** showed similar IR features but were less stable depending on the R′ group. IR data of the products obtained from **32a**^{Co} and **33a**^{Co} suggested formation of a Tp^RCo^I-CO species and reduction to monovalent species upon carbonylation was reported for **35**–**37** coordinated by the ligands bearing bulky *t*-butyl groups.[67,69]

The above three reactions are useful to detect an M–C bond in the Tp^RM-R′-type complexes. Then we tried to trap the thermally unstable ethylnickel complex **34a**^{Ni} by carbonylation (Scheme 18). Treatment of **31a**^{Ni} with EtMgBr at −78 °C gave a green solution, which turned into orange when the mixture was warmed to room temperature. GLC analysis of the gas phase revealed that the warming caused quantitative formation of ethene, while no characterizable Tp^{iPr_2}Ni complex was isolated from the solution as mentioned above. In order to trap the putative ethylnickel intermediate **34a**^{Ni} the green solution was carbonylated at −78 °C and the thermally stable orange diamagnetic product **42** was obtained as a sole organometallic species. The IR [ν(C=O), ν(CO)] and ^{13}C-NMR features [δ_C(C=O), δ_C(CO)] which were similar to those of **39** and **38**, respectively, led to the assignment as the propanoyl complex **42**, Tp^{iPr_2}(CO)Ni–C(=O)–CH$_2$CH$_3$, which was also confirmed by X-ray crystallography. These results confirm that ethylation of **31a**^{Ni} produces the thermally unstable ethyl complex



Scheme 17.



Scheme 18.

$34a^{Ni}$, which, upon warming, undergoes β-hydride elimination never observed for the iron and cobalt systems. The tetrahedral intermediate $34a^{Ni}$ containing the d^8 metal center may be converted to the more stable square-planar species, $Tp^{iPr_2}Ni(H)(CH_2{=}CH_2)$, via β-hydride elimination at a higher temperature.

Oxygenation of the allyl (**32a**) and *p*-methylbenzyl complexes (**33**) afforded acrolein and *p*-tolualdehyde, respectively, in good yields, while the ethyl complexes **34** produced a mixture of oxygenated compounds, i.e. ethanol, acetaldehyde and acetic acid (Scheme 17). When the oxygenation of the η^3-allylcobalt complex $32a^{Co}$ was monitored at −78 °C by UV-vis spectroscopy, a dramatic color change from orange to pale blue was observed upon exposure to O_2. The UV-vis feature of the mixture (λ_{max} 634, 575 nm) similar to those of $Tp^{iPr_2}Co$-OO-cumyl 12^{Co} (λ_{max} 638, 582 nm)[21] suggested conversion of the square-pyramidal species $32a^{Co}$ into a tetrahedral η^1-alkylperoxo intermediate, $Tp^{iPr_2}Co$-OO-allyl, through O_2-insertion into the Co–C bond in $32a^{Co}$.

Reactivity of coordinatively unsaturated organometallic complexes has attracted much attention, because they could be key intermediates of catalytic C–C bond formation. In particular, the recent, independent reports by Brookhart and Gibson[70] on the polymerization catalysts containing PBI [pyridinebis(imine)] ligands with bulky substituents recalled our interest in development of novel catalyst systems based on *N*-coordinated precursors. Both PBI and Tp^R are κ^3-*N*-coordinated ligands but with different coordination geometry, i.e. meridional (PBI) vs facial (Tp^R). In addition, the former ligands are neutral, whereas the latter ligands are monoanionic species. It is therefore interesting to compare their catalytic activity toward olefin polymerization. The results described below, however, show that the Tp^RM complexes are sluggish with respect to C–C bond formation with unsaturated organic compounds including olefin and acetylene.

Toluene solutions containing the ethyl complexes **34a** were heated for 1 hr at 70 °C in the presence of various unsaturated organic compounds. Of the examined organic compounds (ethene, 1-butene, ethyl acrylate, styrene; phenylacetylene, diphenylacetylene; diethylketone; benzonitrile) only phenylacetylene showed indication of some reaction and the other substrates left **34a** unaffected (Scheme 17). The reaction of

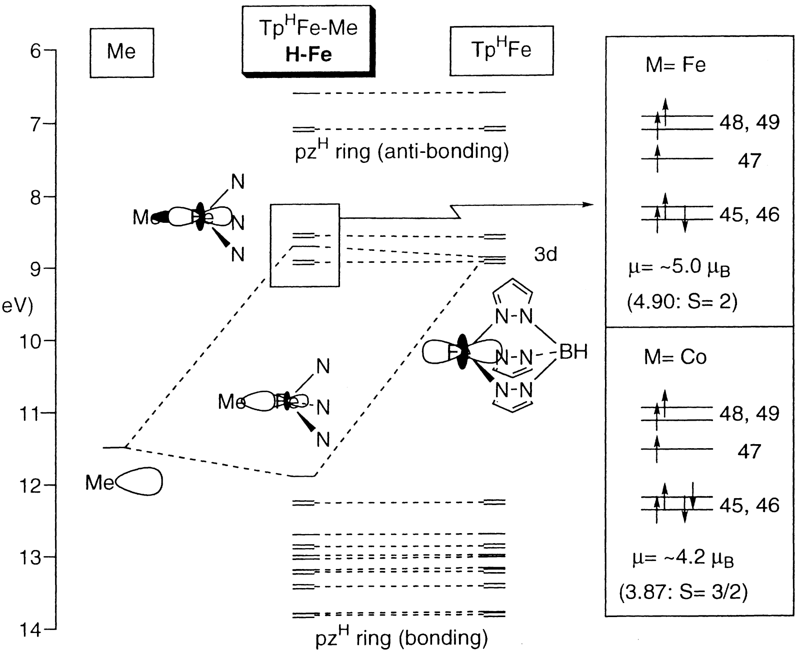


Fig. 5. An MO diagram for Tp^{H}M-Me **H** resulting from the interaction between Me and Tp^{H}M fragments.

the cobalt complex **34a**^{Co} gave an isomeric mixture of *cis*- and *trans*-1-phenyl-1-butene in 68% yield after hydrolysis, indicating formation of the alkenyl complex **40**, which should arise from insertion of the C≡C bond into the Co-Et bond. Reaction of the iron derivative **34a**^{Fe} contrasted with the result of **34a**^{Co}; treatment with phenylacetylene followed by carbonylation gave the diamagnetic product **41**, which was characterized as an acetylide-dicarbonyl complex on the basis of the NMR and IR data. Thus the reaction of **34a**^{Fe} with PhC≡CH should result in protonolysis of the Fe–Et bond by the action of the acidic acetylenic proton followed by coordination of the resulting conjugated base (acetylide ligand) to the metal center to give the acetylide complex, Tp^{iPr_2}Fe–C≡C–Ph.

Preliminary experiments on catalytic ethene polymerization were also carried out using the chloro (**31a**^{Fe} and **31a**^{Co}) and ethyl complexes (**34a**^{Fe} and **34a**^{Co}). Addition of MAO (100 equivalents) caused production of polyethylene but the activities were much smaller ($< 10^{-4}$) than those reported for the PBI catalyst.[70] No evidence for attractive interaction between **34a**^{Co} and ethene was obtained as monitored by ^{1}H NMR (at r.t. and 50 °C). The contrasted catalytic activity for ethene polymerization by the PBI and Tp$^{R'}$ systems suggests that facially coordinated N_3-ligands may not be suitable ancillary ligands for a polymerization catalyst, although some additional experiments are needed to obtain a conclusion.

In order to consider the stability of the hydrocarbyl complexes we performed EHMO calculations for the idealized C_{3v}-symmetrical model methyl complexes, Tp^{H}M-Me **H** (M = Fe, Co). A molecular orbital diagram of **H-Fe** resulting from interaction between the Tp^{H}Fe and Me fragments is shown in Fig. 5. A very similar diagram is obtained for the cobalt complex **H-Co**, and the diagram is essentially the same as those reported for the Tp^{H}Co^{I} species by Theopold et al.[69]

At first glance the diagram is very simple, because the Tp^{H}M fragments have only one σ-type orbital that can interact with the methyl σ-orbital. This situation is in sharp contrast to that of normal organometallic species such as Me-Co(CO)$_4$, where a couple of metal-d-orbital-based orbitals take part in the M–C interaction to form a strong σ bond. As a result, the very small mixing of the orbitals of σ-symmetry in the Tp^{H}M systems renders the bond less covalent. In other words, the M–C bond in **H** is ionic, and this result is in accord with the high sensitivity of Tp^{R}M-R′ toward moisture.

The very small energy separation between frontier orbitals would lead to a high spin configuration as usually observed for tetrahedral metal species.[66] When 6 (Fe) and 7 electrons (Co) are accommodated in the five frontier orbitals, 4 (Fe) and 3 unpaired electrons (Co) will remain in the orbitals 46–49 of higher energies. These pictures of electron configurations are in good agreement with the results of measurements of magnetic moment; the μ_{eff} values [$\sim$5.0 μ_B (Fe), $\sim$4.2 μ_B (Co)] are typical for S = 2 (Fe) and 3/2 (Co).

The electronic configuration displayed in Fig. 5 can also explain the stability of the tetrahedral, "coordinatively unsaturated" species. When the "18e rule"[61] is taken into account, the 14e (**H-Fe**) and 15e species (**H-Co**) are short of valence electrons by 4 and 3 electrons, respectively. But in species **H** all frontier orbitals are occupied either by electron pairs or by unpaired electrons, leaving no vacant frontier (d) orbital for coordination of an additional ligand. The lack of any vacant coordination sites is concluded to be the origin of the stability of the highly "coordinatively unsaturated" organometallic species. It may be impossible for unsaturated hydrocarbons to be coordinated to the metal centers without changing the electronic structure. The electronic structures, however, are not so rigid, because CO, H_2 and O_2 react with these species. Substrates which can perturb the electronic structure of the Tp$^{R'}$M-R complexes may have a chance to show some new reactivity.

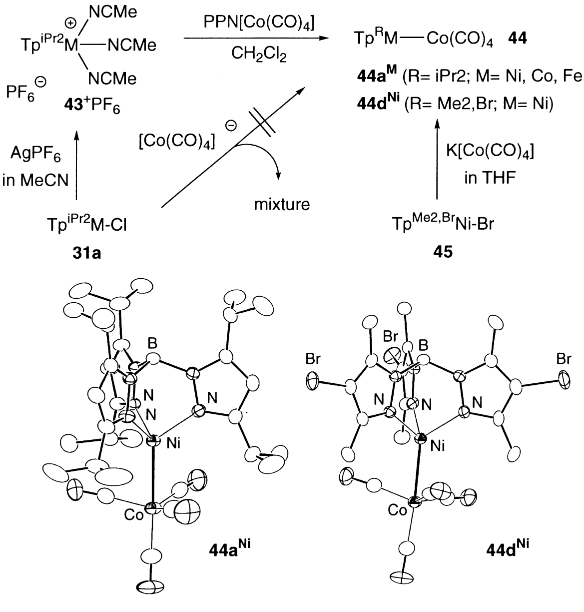
It has been known that carbon ligands cause ligand-field splitting much larger than N-, O- and halo-ligands, which are typical ligands for coordination compounds.[66] The present study reveals that the σ-bonding interaction of carbon ligands is not enough to cause a low-spin configuration with vacant frontier orbitals by lifting up the M-C anti-bonding orbital.

The Tp^R ligand serves as a tetrahedral enforcer in the organometallic system, too, to give the unique highly coordinatively unsaturated hydrocarbyl complexes $\mathrm{Tp}^\mathrm{R}\mathrm{M}$-R′ without any additional stabilizing interaction. The stability has been attributed to the high spin configuration without a vacant frontier orbital resulting from the small ligand field splitting due to the tetrahedral coordination geometry. From the viewpoint of the formal electron-counting, the $\mathrm{Tp}^\mathrm{R}\mathrm{M}$-R′ species are highly coordinatively unsaturated [Fe(14e), Co(15e) << 18e],[61] whereas from the viewpoint of electronic configuration they are coordinatively "saturated" species with no vacant frontier orbital.

3.2. Dinuclear Xenophilic Complex with a Polar Metal–Metal Bond.[71] The successful synthesis of the $\mathrm{Tp}^{i\mathrm{Pr}_2}\mathrm{M}$-R′-type complexes drove us to introduce a metal fragment in place of the hydrocarbyl group (R′). Although a considerable number of polymetallic complexes containing a Tp^R ligand have been reported so far (e.g. Tp^R derivatives of η^5-$\mathrm{C}_5\mathrm{R}_5$-containing cluster complexes), in the previous polymetallic $\mathrm{Tp}^\mathrm{R}\mathrm{M}$ complexes[3] the metal-metal bond is supported by bridging ligands (e.g. μ-CO) or the $\mathrm{Tp}^\mathrm{R}\mathrm{M}$ moiety is coordinatively saturated due to coordination of other auxiliaries (e.g. η^1-CO). To our knowledge no example of well-characterized $\mathrm{Tp}^\mathrm{R}\mathrm{M}$-$\mathrm{M'L}_n$-type complexes containing an unsupported M–M′ bond (M, M′ = transition metal), which could be polar, had been prepared.[72–74] The chemistry of polar metal–metal bonds has attracted increasing attention,[75] because they are expected to display structural and reaction features based on the cooperativity of the two metal centers with different properties. In particular, so-called "xenophilic" species[76] having a polar bond between a Werner complex type hard open-shell metal center and a metal carbonyl fragment are now recognized as a new class of polymetallic complexes but they are still rare.

Treatment of the labile cationic solvated complexes, $[\mathrm{Tp}^{i\mathrm{Pr}_2}\mathrm{M(NCMe)}_3]^+$ **43**$^+$, with PPN[Co(CO)$_4$] afforded the dinuclear complexes $\mathrm{Tp}^{i\mathrm{Pr}_2}\mathrm{M}$-$\mathrm{Co(CO)}_4$ **44**, in moderate yields (Scheme 19). Attempted preparation from the chloro complexes **31a** resulted in the formation of cationic aquo or carbonato complexes containing $[\mathrm{Co(CO)}_4]^-$ as the counteranion[77] after a prolonged reaction period as a result of interaction with adventitious moisture or carbon dioxide in the basic reaction media. The reaction of the bromo complex **45**, bearing the less bulky methyl-substituted ligand, however, produced the corresponding dinuclear complex **43d**$^\mathbf{Ni}$ in contrast to the sluggishness of **31a**$^\mathbf{Ni}$, which could be ascribed to the bulkiness and the electron-donating property of the $\mathrm{Tp}^{i\mathrm{Pr}_2}$ ligand. Although complexes **44a** and **44d**$^\mathbf{Ni}$ are air- and moisture-sensitive, no significant difference has been observed for their thermal stabilities. Therefore, kinetic stabilization is not essential for the metal-metal bond formation in $\mathrm{Tp}^\mathrm{R}\mathrm{M}$-$\mathrm{Co(CO)}_4$ as in the case of the hydrocarbyl complexes mentioned above.

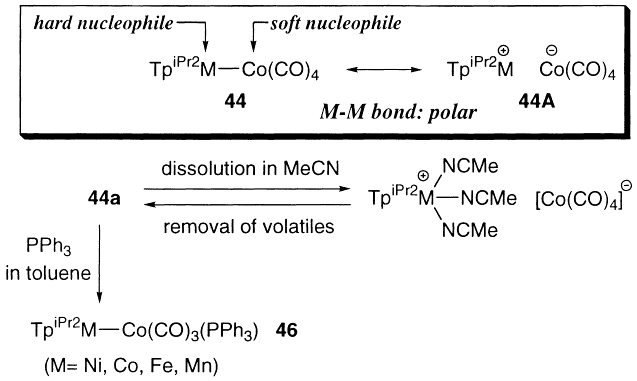
The dinuclear complexes **44a** and **44d**$^\mathbf{Ni}$ were characterized by IR [ν_CO pattern peculiar to C_{3v}-symmetrical X-Co(CO)$_4$ species and ν_BH (2530 cm^{-1}) indicative of κ^3-$\mathrm{Tp}^{i\mathrm{Pr}_2}$ coordination][42] and X-ray crystallography (Scheme 19). The five complexes prove to be isostructural, and ORTEP views of **44a**$^\mathbf{Ni}$ and **44d**$^\mathbf{Ni}$ show the virtually C_3-symmetrical structures with the staggered conformation of the three pz^R rings and the three equatorial CO ligands. It should be noted that the Co–Co distance in **44a**$^\mathbf{Co}$ [2.4969(8) Å] is comparable to the covalent Co–Co bond length found in $\mathrm{Co}_2(\mathrm{CO})_8$ with two μ-CO ligands (2.522 Å)[78] and the other M–Co distances also fall in the range of single bond lengths [2.4640(8) (**44a**$^\mathbf{Ni}$), 2.504(1) (**44a**$^\mathbf{Fe}$), 2.581(1) (**44a**$^\mathbf{Mn}$), 2.4190(9) Å (**44d**$^\mathbf{Ni}$)]. In the series of the **44a**-type complexes the increase of the M–Co and M–N distances is associated with that of the atomic radius of M but no apparent systematic change is observed for other structural parameters. Although the equatorial CO ligands are tilted toward the nickel center, the linear Co–C–O linkage (175.7–178.3°) and the Ni···CO distances longer than 2.6 Å reveal that the CO ligands are η^1-bonded to Co1 without any bonding interaction with M, leaving the $\mathrm{Tp}^\mathrm{R}\mathrm{M}$ moiety electron-deficient as in the alkyl complexes. Thus the dinuclear complexes **44** turn out to be xenophilic complexes with 29 (Mn), 30 (Fe), 31 (Co) and 32 (Ni) valence electrons (cf. 34e for coordinatively saturated dinuclear species) consisting of the electron-deficient $\mathrm{Tp}^\mathrm{R}\mathrm{M}$ moiety and the coordinatively saturated Co(CO)$_4$ moiety.



Scheme 19.

Previous examples of xenophilic complexes resulted from a series of complicated redox disproportionations of metal carbonyls and no rational systematic synthetic method has been developed. Our study on **44** reveals that the Tp^R ligand recognized as a tetrahedral enforcer is a versatile ancillary ligand for the "hard" part in heterometallic xenophilic complexes. The homometallic complex **44a**$^\mathbf{Co}$ is isoelectronic with the cationic part of $[(\mathrm{py})_3\mathrm{Co}$-$\mathrm{Co(CO)}_4]^+[\mathrm{Co(CO)}_4]^-$ reported by Fachinetti,[76a] which is regarded as the first example of a xenophilic complex.[76b]

The M–M bonds in **44** are polar as indicated by their CO vibrations and Co–CO distances, which are intermediate between those for R-Co$^\mathrm{I}$(CO)$_4$ with a covalent Co–C bond [R = phthalimidoylmethyl; 2107, 2040, 2029, 2020 cm^{-1};[79a] 1.818 (axial), 1.802 Å (equatorial)[79b]][79a] and the ionic species, $[\mathrm{Co}^{-\mathrm{I}}(\mathrm{CO})_4]^-$ [1880 cm^{-1};[79c] 1.756 Å[79b]].[79d] The polar nature



Scheme 20.

of the M–M bond, which is interpreted in terms of contribution of the ionic form **44A** (Scheme 20), is also verified by a chemical reaction. Dissolution of **44** in MeCN reversed the metal-metal bond formation to give the ion pair $[\mathrm{Tp}^{i\mathrm{Pr}_2}\mathrm{M}(\mathrm{NCMe})_3]^+[\mathrm{Co(CO)}_4]^-$, UV-vis and IR features of which were identical with those of the starting compounds, $\mathbf{43}^+$ (UV-vis) and PPN[$\mathrm{Co(CO)}_4$] (IR; ν_{CO}), confirming the presence of the corresponding metallic components in the solution (Scheme 20). Removal of the volatiles under reduced pressure regenerated **44**, although partial decomposition was evident. The bond heterolysis should be promoted by nucleophilic attack of MeCN at the positively charged $\mathrm{Tp}^{i\mathrm{Pr}_2}$M moiety in **44** and ionic cleavage of a metal–metal bond has several precedents.[80] Contrastingly, addition of PPh_3 to **44** resulted in selective CO-displacement at the $\mathrm{Co(CO)}_4$ moiety to give the substituted products **46**. These results reveal the ambident character of **1**; hard and soft nucleophiles attack the hard open-shell Tp^{R}M moiety and the metal carbonyl fragment, respectively, in a specific manner. The core part of the phosphine-substituted heterometallic complex **46a** characterized crystallographically is isostructural with that of **44a**, while the Ni–Co distance in $\mathbf{46a}^{\mathrm{Ni}}$ [2.4138(9) Å] is shorter than that in $\mathbf{44a}^{\mathrm{Ni}}$ due to an increase of electron density at the $\mathrm{Co(CO)}_3\mathrm{L}$ moiety causing an increase of the Co-to-M donation, i.e. the covalent character of the Co–M bond. The M–Co bond in **46a**, however, was also cleaved in a $\mathrm{CH_3CN}$-containing solvent system.

The successful synthesis of the unique dinuclear xenophilic complexes **44** is realized by the use of the tetrahedral enforcer Tp^{R}. Further study on the reactivity of the obtained xenophilic species is now under way.

4. Concluding Remarks

The results of our recent research on the inorganic chemistry of the Tp^{R}M complexes are summarized. The Tp^{R} ligand proves to be so versatile as to be used for a wide range of the studies extending from bioinorganic chemistry to organometallic chemistry, which have revealed the following new aspects in addition to the features discussed in the introductory part.

1. The most significant feature of the facial Tp^{R} ligand system is that, for first row transition metal complexes, Tp^{R} serves as "a tetrahedral enforcer" to form a coordinatively unsaturated tetrahedral species; such a property is best demonstrated in organometallic systems. In the case of Tp^{R}M-X complexes, where X ($\mathrm{NR'_2}$, OR′, halide) has lone pair electrons, the coordinatively unsaturated metal center may be stabilized by π-donation of the electron pair of X to the metal center or by formation of an oligomeric structure with X-bridge(s) (as in **2**). In contrast to these complexes, such stabilization is not working for the hydrocarbyl complexes, in particular, the ethyl complex, but still such species are thermally stable even in the absence of kinetic stabilization by a bulky Tp^{R} ligand. This is the definite evidence for the property of Tp^{R} as a tetrahedral enforcer.

2. The tetrahedral structure is readily interconverted with the five- or six-coordinate structure through addition/dissociation of donor(s). Structural flexibility (lability) is the key feature of first row transition metal Tp^{R} complexes and the structural change should be associated with variation of the physicochemical properties (e.g. redox property) and chemical reactivities. These features should play significant roles in controlling functions of first row transition metal complexes. Functions of metalloenzymes containing first row transition metals should be presumably controlled by similar principles.

3. In contrast to the first row transition metal species, second row transition metal complexes obey the "18-electron (or EAN) rule" and don't form a tetrahedral structure. d^8 Metals (e.g. $\mathrm{Pd^{II}}$, $\mathrm{Rh^{III}}$) form a 16e square-planar species with a κ^2-Tp^{R} ligand and such a coordinatively unsaturated species can be an active species of stoichiometric and catalytic transformations. Actually the Rh-O_2 complex was obtained by oxidative addition to a 16e species. The κ^2- and κ^3-forms readily interconvert with each other through coordination/dissociation of the axial pz^{R} group and can be readily discriminated by the ν(B-H) value.

4. Extension of the central metal in the dinuclear μ-O_2 complex, $\mathrm{Tp}^{\mathrm{R}}\mathrm{M}(\mu\text{-}\mathrm{O}_2)\mathrm{MTp}^{\mathrm{R}}$, to those irrelevant to the biological system leads to the discovery of the higher valent dinuclear bis(μ-oxo) species, $\mathrm{Tp}^{\mathrm{R}}(\mu\text{-O})_2\mathrm{MTp}^{\mathrm{R}}$, resulting from O–O scission of the μ-η^2:η^2-peroxo intermediate. The unique structural and spectral features of the bis(μ-oxo) species are fully characterized, and product and kinetic analyses of the thermal decomposition processes reveal that the oxygenation is initiated by H-abstraction of a C–H bond of the R^3 substituent by the bridging O-group with oxyl radical character. The analogous intermediate Q is proposed as the key intermediate of the oxygenation mediated by *methane monooxygenase*.

5. Synthetic study of second row transition metal-dioxygen complexes shows that they are much more thermally stable than the first row transition metal complexes and such study provides us with structural information concerning the peroxo species. A variety of peroxo [η^2-O_2 (Rh), μ-η^1:η^1-O_2, μ-η^1:η^2-O_2 (Pd_2)], alkylperoxo (Pd) and hydroperoxo complexes (Pd, Rh) have been prepared and fully characterized. Although the M-OOH species are proposed as intermediates of oxygenation reactions, only a limited number of fully characterized examples have been reported so far. The Rh-OOH complex is formed by O_2-oxidative addition to a low valent metal species followed by ring-opening protonation of the resultant cyclic η^2-peroxo intermediate. This result provides the first structural support for the activation mechanism of *cyctochrome P-450*, which has been supported by spectroscopic characterization of the intermediates.

6. Introduction of hydrocarbyl ligand into the C_{3v}-symmetri-

cal Tp$^{\mathrm{R}}$M system furnishes the tetrahedral, highly electron-deficient hydrocarbyl complexes, Tp$^{\mathrm{R}}$M-R′, with 14 (Fe) and 15 (Co) valence electrons. Despite the electron-deficient nature of the organometallic species they are thermally stable with respect to β-hydrogen elimination but their reactivity toward organic substrates including alkene and alkyne turns out to be sluggish. These chemical properties have been ascribed to the high spin electron configuration without any vacant frontier orbital; such an electronic configuration results from the small ligand field splitting caused by the tetrahedral structure. Analogous dinuclear complexes, Tp$^{\mathrm{R}}$M–M′L$_n$ with a polar metal–metal bond, so-called xenophilic complexes, have also been successfully isolated and fully characterized.

These results clearly indicate that the unique features of the Tp$^{\mathrm{R}}$ ligand mentioned above lead to the successful formation and intriguing properties of the bioinorganic and organometallic complexes.

We gratefully acknowledge the former and present students, whose names appear in our publications, for their contributions to the study described above. We thank Professor Emeritus Yoshihiko Moro-oka (the former head of our division) for his support and encouragement. We are also grateful to the financial support from the Ministry of Education, Science, Sports, Culture and Technology (Grant-in-Aid for Scientific Research: No. 11228201).

References

1 a) S. Trofimenko, *J. Am. Chem. Soc.*, **88**, 1842 (1966). b) S. Trofimenko, *Inorg. Synth.*, **12**, 99 (1970).

2 Abbreviations used in this paper: Tp$^{\mathrm{R}}$: hydrotris(pyrazolyl)borato ligands; Tp$^{i\mathrm{Pr}_2}$: 3,5-diisopropylpyrazolyl derivative; Tp$^{\mathrm{Me}_2}$: 3,5-dimethylpyrazolyl derivative; Tp$^{\mathrm{Me}_3}$: 3,4,5-trimethylpyrazolyl derivative; Tp$^{\mathrm{Me}_2,\mathrm{Br}}$: 3,5-dimethyl-4-bromopyrazolyl derivative; Tp$^{\mathrm{Me}_2,\mathrm{X}}$: 3,5-trimethyl-4-X-pyrazolyl derivative (X: Me, H, Br); Tp$^{\mathrm{H}}$: the non-substituted parent ligand; pz$^{\mathrm{R}}$: pyrazolyl group in Tp$^{\mathrm{R}}$. For compounds, **1**–**3**, **10**, **12**, **31**–**34**, **43**, **44** and **46**, compound numbers without the name of the central metal atom refer to the series of metal complexes of a certain structure and each metal derivative is specified by the superscript. For example, **2a** stands for the series of (Tp$^{i\mathrm{Pr}_2}$M)$_2$(μ-OH)$_2$-type complexes of various metals, whereas **2a**$^{\mathbf{Ni}}$ stands for the nickel derivative, (Tp$^{i\mathrm{Pr}_2}$Ni)$_2$(μ-OH)$_2$.

3 a) S. Trofimenko, "Scorpionates - The Coordination Chemistry of Polypyrazolylborate Ligands," Imperial College Press, London (1999). b) S. Trofimenko, *Chem. Rev.* **93**, 943 (1993).

4 N. Kitajima and W. B. Tolman, *Prog. Inorg. Chem.*, **43**, 419 (1995).

5 F. Malbosc, P. Kalck, J.-D. Daran, and M. Etienne, *J. Chem. Soc., Dalton Trans.*, **1999**, 271. M. Paneque, S. Sirol, M. Trujillo, E. Gutiérrez-Puebla, M. A. Monge, and E. Carmona, *Angew. Chem., Int. Ed.*, **39**, 218 (2000). κ^4-Tp$^{\mathrm{R}}$ is known; see Ref. 55b).

6 See the figure on the jacket of Ref. 3.

7 Cone angles are estimated for thallium compounds (Tp$^{\mathrm{R}}$Tl): Tp$^{\mathrm{H}}$: 183°; Tp$^{\mathrm{Me}_2}$: 239°; Tp$^{3\text{-}t\mathrm{Bu}}$: 251°; Tp$^{3\text{-cyclohexyl}}$: 281°. See Ref. 3a.

8 See the introductory part of the following paper: M. Akita, D.-q. Ma, S. Hikichi, and Y. Moro-oka, *J. Chem. Soc., Dalton Trans.*, **1999**, 987. See also, D.-q. Ma, S. Hikichi, M. Akita and Y. Moro-oka, *J. Chem. Soc., Dalton Trans.*, **2000**, 1123.

9 J. P. Jesson, S. Trofimenko, and D. R. Eaton, *J. Am. Chem. Soc.*, **89**, 3148 (1967).

10 W. Kläui and H. Hamers, *J. Organomet. Chem.*, **345**, 287 (1988).

11 N. Kitajima and Y. Moro-oka, *Chem. Rev.*, **94**, 737 (1994); M. Akita, K. Fujisawa, S. Hikichi, and Y. Moro-oka, *Res. Chem. Interm.*, **24**, 291 (1998); M. Akita, S. Hikichi, and Y. Moro-oka, *J. Synth. Org. Chem.*, **57**, 619 (1998) (in Japanese).

12 a) N. Kitajima, K. Fujisawa, and Y. Moro-oka, *J. Am. Chem. Soc.*, **111**, 8975 (1989). b) N. Kitajima, K. Fujisawa, C. Fujimoto, Y. Moro-oka, S. Hashimoto, T. Kitagawa, K. Toriumi, K. Tatsumi, and A. Nakamura, *J. Am. Chem. Soc.*, **114**, 1277 (1992).

13 a) H. Suzuki, K. Mizutani, Y. Moro-oka, and T. Ikawa, *J. Am. Chem. Soc.*, **101**, 748 (1979). b) F. Sakurai, H. Suzuki, Y. Moro-oka, and T. Ikawa, *J. Am. Chem. Soc.*, **102**, 1749 (1980).

14 a) K. A. Magnus, B. Hazes, H. Ton-That, C. Bonaveture, J. Bonaveture, and W. G. J. Hol, *Proteins*, **19**, 302 (1994). b) K. A. Magnus, H. Ton-That, and J. E. Carpenter, *Chem. Rev.*, **94**, 727 (1994).

15 Special thematic issue of *Chem. Rev.* for "Bioinorganic Enzymology," *Chem. Rev.*, **96**, 2237–3042 (1996). S. J. Lippard and J. M. Berg. "Principles of Bioinorganic Chemistry," University Science Books, CA (1994).

16 a) R. A. Sheldon and J. K. Kochi, "Metal-Catalyzed Oxidations of Organic Compounds," Academic Press, New York (1981). b) S. Patai, "The chemistry of peroxides," John Wiley & Sons, Chichester (1983). c) A. E. Martel and D. T. Sawyer, "Oxygen Complexes and Oxygen Activation by Transition Metals," Plenum Press, New York (1988). d) W. Ando, "Organic Peroxides," John Wiley and Sons, Chichester (1992). e) Thematic issue of *Chem. Rev.* (Metal-Dioxygen Complexes), *Chem. Rev.*, **94**, 567 (1994). f) G. Strukul, *Angew. Chem., Int. Ed.*, **37**, 1198 (1998). g) S. Murahashi, *Angew. Chem., Int. Ed. Engl.*, **34**, 2443 (1995). h) Y. Moro-oka and M. Akita, *Catal. Today*, **41**, 217 (1998). i) M. Akita and Y. Moro-oka, *Catal. Today*, **44**, 183 (1998).

17 a) S. Hikichi, M. Yoshizawa, Y. Sasakura, M. Akita, and Y. Moro-oka, *J. Am. Chem. Soc.*, **120**, 10567 (1998). b) S. Hikichi, M. Yoshizawa, Y. Sasakura, H. Komatsuzaki, Y. Moro-oka, and M. Akita, *Chem. Eur. J.*, **7**, 5011 (2001). c) S. Hikichi, M. Akita, and Y. Moro-oka, *Coord. Chem. Rev.*, **198**, 61 (2000).

18 N. Kitajima, S. Hikichi, M. Tanaka, and Y. Moro-oka, *J. Am. Chem. Soc.*, **115**, 5496 (1993).

19 N. Kitajima,; U. P. Singh, H. Amagai, M. Osawa, and Y. Moro-oka, *J. Am. Chem. Soc.*, **113**, 7757 (1991).

20 S. Hikichi, H. Komatsuzaki, N. Kitajima, M. Akita, M. Mukai, T. Kitagawa, and Y. Moro-oka, *Inorg. Chem.*, **36**, 266 (1997).

21 S. Hikichi, H. Komatsuzaki, M. Akita, and Y. Moro-oka, *J. Am. Chem. Soc.*, **120**, 4699 (1998).

22 S. Itoh, H. Bandoh, S. Nagatomo, T. Kitagawa, and S. Fukuzumi, *J. Am. Chem. Soc.*, **121**, 8945 (1999). K. Shiren, S. Ogo, S. Fujinami, H. Hayashi, M. Suzuki, A. Uehara, Y. Watanabe, and Y. Moro-oka, *J. Am. Chem. Soc.*, **122**, 254 (2000). B. S. Mandimutsira, J. L. Yamarik, T. C. Brunold, W. Gu, Stephen P. Cramer, and C. G. Riordan, *J. Am. Chem. Soc.*, **123**, 9194 (2001).

23 a) TACN$^{\mathrm{R}}$: 1,4,7-trisubstituted 1,4,7-triazacyclononane. b) J. A. Halfen, S. Mahapatra, E. C. Wilkinson, S. Kaderli, V. G.

Young, Jr., L. Que, Jr., A. D. Zuberbühler, and W. B. Tolman, *Science*, **271**, 1397 (1996). c) S. Mahapatra, J. A. Halfen, E. C. Wilkinson, G. Pan, X. Wang, V. G. Young, Jr., C. J. Cramer, L. Que, Jr., and W. B. Tolman, *J. Am. Chem. Soc*., **118**, 11555 (1996).

24 M. J. Henson, P. Mukherjee, D. E. Root, T. D. P. Stack, and E. I. Solomon, *J. Am. Chem. Soc*., **121**, 10332 (1999).

25 a) P. B. Hitchcock and G. M. McLaughlin, *J. Chem. Soc., Dalton Trans*., **1976**, 1927. b) N. A. Bailey, E. D. McKenzie, and J. M. Worthington, *J. Chem. Soc., Dalton Trans*., **1977**, 763. c) L. H. Doerrer, M. T. Bautista, and S. J. Lippard, *Inorg. Chem*., **36**, 3578 (1997). d) M. D. Fryzuk, D. B. Leznoff, R. C. Thompson, and S. J. Rettig, *J. Am. Chem. Soc*., **120**, 10126 (1998). e) B. S. Hammes, V. G.Young, Jr., and A. S. Borovik, *Angew. Chem., Int. Ed*., **38**, 666 (1999).

26 M. J. Baldwin, D. E. Root, J. E. Pate, K. Fujisawa, N. Kitajima, and E. I. Solomon, *J. Am. Chem. Soc*., **114**, 10421 (1992).

27 S. Hikichi, M. Yoshizawa, Y. Sasakura, H. Komatsuzaki, M. Akita, and Y. Moro-oka, *Chem. Lett*., **1999**, 979.

28 a) O. M. Reinaud and K. H. Theopold, *J. Am. Chem. Soc*., **116**, 6979 (1994). b) O. M. Reinaud, G. P. A. Yap, A. L. Rheingold, and K. H. Theopold, *Angew. Chem., Int. Ed*., **34**, 2051 (1995). c) K. H. Theopold, O. M. Reinaud, D. Doren, and R. Konecny, in "3rd World Congress on Oxidation Catalysis," ed by R. K. Grasselli, S. T. Oyama, A. M. Gaffney, and J. E. Lyons, Elsevier, Amsterdam (1997), pp. 1081–1088.

29 S. Mahapatra, J. A. Halfen, E. C. Wilkinson, L. Que, Jr., and W. B. Tolman, *J. Am. Chem. Soc*., **116**, 9785 (1994).

30 See Ref. 16c and references cited therein.

31 Cu: a) H. V. Obias, Y. Lin, N. N. Murthy, E. Pidcock, E. I. Solomon, M. Ralle, N. J. Blackburn, Y.-M. Neuhold, A. D. Zuberbühler, and K. D. Karlin, *J. Am. Chem. Soc*., **120**, 12960 (1998). Fe: b) C. Kim, Y. Dong, and L. Que, Jr., *J. Am. Chem. Soc*., **119**, 3635 (1997). Mn: c) K. Wang and J. M. Mayer, *J. Am. Chem. Soc*., **119**, 1470 (1997).

32 a) M. Merkx, D. A. Kopp, M. H. Sazinsky, J. L. Blazyk, J. Müller, and S. J. Lippard, *Angew. Chem., Int. Ed*., **20**, 2782 (2001). b) B. J. Wallar and J. D. Lipscomb, *Chem. Rev*., **96**, 2625 (1996). c) A. M. Valentine and S. J. Lippard, *J. Chem. Soc., Dalton Trans*., **1997**, 3925. d) L. Shu, J. C. Nesheim, K. Kauffmann, E. Münck, J. D. Lipscomb, and L. Que, Jr., *Science*, **275**, 515 (1997). e) A. M. Valentine, S. S. Stahl, and S. J. Lippard, *J. Am. Chem. Soc*., **121**, 3876 (1999).

33 a) W. B. Tolman, *Acc. Chem. Res*., **30**, 227 (1997). b) P. Holland and W. B. Tolman, *Coord. Chem. Rev*., **190–192**, 855 (1999). c) L. Que, Jr. and Y. Dong, *Acc. Chem. Res*., **29**, 190 (1996). d) L. Que, Jr., *J. Chem. Soc., Dalton Trans*., **1997**, 3933.

34 Mn: a) H. Komatsuzaki, S. Hikichi, M. Akita, and Y. Moro-oka, *Inorg. Chem*., **37**, 6554 (1998). Fe: b) T. Ogihara, S. Hikichi, M. Akita, T. Uchida, T. Kitagawa, and Y. Moro-oka, *Inorg. Chim. Acta*, **297**, 162 (2000). Ni: c) S. Hikichi, Y. Ohzu, H. Komatsuzaki, Y. Moro-oka, and M. Akita, to be reported. Co: d) Ref. 21. Cu: e) N. Kitajima, T. Katayama, K. Fujisawa, Y. Iwata, and Y. Moro-oka, *J. Am. Chem. Soc*., **115**, 7872 (1993).

35 a) E. N. Jacobsen, "Comprehensive Organometallic Chemistry II," ed by E. Abel, F. G. A. Stone, and G. Wilkinson, Pergamon, New York (1995), vol.12, pp. 1097–1135. b) A. E. Shilov and G. B. Shul'pin, *Chem. Rev*., **97**, 2879 (1997). c) S. S. Stahl, J. A. Labinger, and J. E. Bercaw, *Angew. Chem., Int. Ed*., **37**, 5000 (1998).

36 a) T. Katsuki and K. B. Sharpless, *J. Am. Chem. Soc*., **102**, 5974 (1980). b) I. D. Williams, S. F. Pedersen, K. B. Sharpless, and S. J. Lippard, *J. Am. Chem. Soc*., **106**, 6430 (1984). c) T. Katsuki and V. S. Martin, *Org. React*., **48**, 1 (1996).

37 Ti: a) G. Boche, K. Möbus, K. Harms, and M. Marsch, *J. Am. Chem. Soc*., **118**, 2770 (1996). Hf: b) A. van Asselt, B. D. Santarsiero, and J. E. Bercaw, *J. Am. Chem. Soc*., **108**, 8291 (1986). V: c) H. Mimoun, P. Chaumette, M. Mignard, L. Saussine, J. Fischer, and R. Weiss, *Nouv. J. Chim*., **7**, 467 (1983). Fe: d) J.-J. Girerd, F. Banse, and A. J. Simaan, *Struct. Bonding*, **97**, 145 (2000). Co: e) F. A. Chavez and P. K. Mascharak, *Acc. Chem. Res*., **33**, 539 (2000). Pd, Pt: f) H. Mimoun, R. Charpentier, A. Mitschler, J. Fischer, and R. Weiss, *J. Am. Chem. Soc*., **102**, 1047 (1980).

38 S. Hikichi, T. Ogihara, K. Fujisawa, N. Kitajima, M. Akita, and Y. Moro-oka, *Inorg. Chem*., **36**, 4539 (1997).

39 T. Ogihara, S. Hikichi, M. Akita, and Y. Moro-oka, *Inorg. Chem*., **37**, 2614 (1998).

40 M. Kosugi, S. Hikichi, M. Akita, and Y. Moro-oka, *J. Chem. Soc., Dalton Trans*., **1999**, 1369. M. Kosugi, S. Hikichi, M. Akita, and Y. Moro-oka, *Inorg. Chem*., **38**, 2567 (1999).

41 N. Kitajima, H. Komatsuzaki, S. Hikichi, M. Osawa, and Y. Moro-oka, *J. Am. Chem. Soc*., **116**, 11596 (1994). H. Komatsuzaki, Y. Nagasu, K. Suzuki, T. Shibasaki, M. Satoh, F. Ebina, S. Hikichi, M. Akita, and Y. Moro-oka, *J. Chem. Soc., Dalton Trans*., **1998**, 511. H. Komatsuzaki, S. Ichikawa, S. Hikichi, M. Akita, and Y. Moro-oka, *Inorg. Chem*., **37**, 3652 (1998). U. P. Singh, R. Singh, S. Hikichi, M. Akita, and Y. Moro-oka, *Inorg. Chim. Acta*, **310**, 273 (2000).

42 M. Akita, K. Ohta, Y. Takahashi, S. Hikichi and Y. Moro-oka, *Organometallics*, **16**, 4121 (1997).

43 ^{15}N-NMR: a) U. E. Bucher, A. Currao, R. Nesper, H. Rüegger, L. M.Venanzi, and E. Younger, *Inorg. Chem*., **34**, 66 (1995). ^{11}B-NMR: b) T. O. Northcutt, R. J. Lachicotte, and W. D. Jones, *Organometallics*, **17**, 5148 (1998).

44 a) M. Akita, T. Miyaji, S. Hikichi, and Y. Moro-oka, *J. Chem. Soc., Chem. Commun*., **1998**, 1005. b) M. Akita, T. Miyaji, S. Hikichi, and Y. Moro-oka, *Chem. Lett*., **1999**, 813. c) M. Akita, T. Miyaji, N. Muroga, C. Mock-Knoblauch, S. Hikichi, W. Adam, and Y. Moro-oka, *Inorg. Chem*., **39**, 2096 (2000).

45 T. Miyaji, S. Hikichi, Y. Moro-oka, and M. Akita, Submitted for publication.

46 Structure detrmination of a tetrameric μ-tert-butylperoxopalladium complex [Pd(μ-O$_2$CCl$_3$)(μ-OOBu^t)]$_4$ [O–O 1.49 Å; mean Pd–O 1.994(3) Å; H. Mimoun, R. Charpentier, A. Mitschler, J. Fischer, and R. Weiss, *J. Am. Chem. Soc*., **102**, 1047 (1980)] and a monomeric η^2-peroxo complex, (η^2-O$_2$)Pd(PBu$^t_2$Ph)$_2$ [O–O 1.37(2) Å, Pd–O 2.051(14), 2.057(12) Å; T. Yoshida, K. Tatsumi, M. Matsumoto, K. Nakatsu, A. Nakamura, T. Fueno, and S. Otsuka, *Nouv. J. Chim*., **3**, 761 (1979)] was reported.

47 M. Kujime, S. Hikichi, and M. Akita, Submitted for publication.

48 Y. Takahashi, M. Hashimoto, S. Hikichi, M. Akita, and Y. Moro-oka, *Angew. Chem., Int. Ed*., **38**, 3074 (1999).

49 a) ref. 42. b) K. Ohta, M. Hashimoto, Y. Takahashi, S. Hikichi, M. Akita, and Y. Moro-oka, *Organometallics*, **18**, 3234 (1999). c) M. Akita, M. Hashimoto, S. Hikichi and Y. Moro-oka, *Oganometallics*, **19**, 3744 (2000).

50 U. Thewalt and R. Marsh, *J. Am. Chem. Soc*., **89**, 6364 (1967). J.-M. Le Carpentier, A. Mitschler, and R. Weiss, *Acta Crystallogr. Sect. B*, **28**, 1288 (1972). D. Carmona, M. P. Lamata,

J. Ferrer, J. Modrego, M. Perales, F. J. Lahoz, R. Atencio, and L. A. Oro, *J. Chem. Soc., Chem. Commun.*, **1994**, 575. A. Wada, M. Harata, K. Hasegawa, K. Jitsukawa, H. Masuda, M. Mukai, T. Kitagawa, and H. Einaga, *Angew. Chem., Int. Ed.*, **37**, 798 (1998). D. D. Wick and K. I. Goldberg, *J. Am. Chem. Soc.*, **121**, 11900 (1999). I. A.Guzei and A. Bakac, *Inorg. Chem.*, **40**, 2390 (2001).

51 Fe: a) R. M. Burger, *Chem. Rev.*, **98**, 1153 (1998). b) F. Neese, J. M. Zaleski, K. L. Zaleski, and E. I. Solomon, *J. Am. Chem. Soc.*, **122**, 11703 (2000). K. Chen, and L. Que, Jr., *J. Am. Chem. Soc.*, **123**, 6327 (2001). Cu: c) J. P. Klinman, *Chem. Rev.*, **96**, 2541 (1996). d) S. T. Prigge, A. S. Kolhekar, B. A. Eipper, R. E. Mains, and L. M. Amzel, *Science*, **278**, 1300 (1997). e) T. Ohta, T. Tachiyama, K. Yoshizawa, T. Yamabe, T. Uchida, and T. Kitagawa, *Inorg. Chem.*, **39**, 4358 (2000).

52 A related protonation reaction of the peroxorhodium complex, RhCl(η^2-O_2)(PPh_3)$_3$, with acac-H giving RhCl(OOH)(PPh_3)$_2$(acac), was reported. a) H. Suzuki, S. Matsuura, Y. Moro-oka, and T. Ikawa, *Chem. Lett.*, **1982**, 1011. b) H. Suzuki, S. Matsuura, Y. Moro-oka, and T. Ikawa, *J. Organomet. Chem.*, **286**, 247 (1985). Similar O_2-O_2H ligand interconversion via protonation-deprotonation processes has been reported for non-heme model systems but the M-O_2 and M-O_2H species were identified spectroscopically. c) R. Y. N. Ho, G. Roelfes, R. Hermant, R. Hage, B. L. Feringa and L. Que, Jr., *J. Chem. Soc., Chem. Commun.*, **1999**, 2161. d) F. Neese and E. I. Solomon, *J. Am. Chem. Soc.*, **120**, 12829 (1998). e) K. B. Jensen, C. J. McKenzie, L. P. Nielsen, J. Z. Pedersen and H. M. Svendsen, *J. Chem. Soc., Chem. Commun.*, **1999**, 1313. f) A. J. Simaan, F. Banse, P. Mialane, A. Boussac, S. Un, T. Kargar-Grisel, G. Bouchoux and J.-J. Girerd, *Eur. J. Inorg. Chem.*, **1999**, 993. g) A. J. Simaan, F. Banse, J.-J. Girerd, K. Wieghardt and E. Bill, *Inorg. Chem.*, **40**, 6538 (2001).

53 a) R. Sato and T. Omura, "Cytochrome P-450," Kodansha, Tokyo (1978). b) P. R. O. de Montellano, "Cytochrome P-450: Structure, Mechanism and Biochemistry, Plenum," New York (1986). c) Y. Watanabe and J. T. Groves, "The Enzymes," ed by B. Sigman, Academic, Orlando (1992). d) M. Sono, M. P. Roach, E. D. Coulter, and J. H. Dawson, *Chem. Rev.*, **96**, 2625 (1996).

54 Y. Takahashi, S. Hikichi, M. Akita, and Y. Moro-oka, *Chem. Commun.*, 1491 (1999).

55 a) Y. Takahashi, M. Akita, S. Hikichi, and Y. Moro-oka, *Inorg. Chem.*, **37**, 3186 (1998). b) Y. Takahashi, M. Akita, S. Hikichi, and Y. Moro-oka, *Organometallics*, **17**, 4884 (1998).

56 M. Akita, Y. Takahashi, S. Hikichi, and Y. Moro-oka, *Inorg. Chem.*, **40**, 169 (2001).

57 Y. Takahashi, S. Hikichi, M. Akita, and Y. Moro-oka, *Organometallics*, **18**, 2571 (1999).

58 K. Kirchner, K. Mauthner, K. Mereiter, and R. Schmid, *J. Chem. Soc., Chem. Commun.*, 892 (1993). I de los Rios, M. J. Tenorio, J. Padilla, M. P. Puerta, and P. Valerga, *J. Chem. Soc., Dalton Trans.*, **1996**, 377. M. Sato and M. Asai, *J. Organomet. Chem.*, **508**, 121 (1996).

59 According to the EL values defined and determined by Lever, the order of electron-donating ability is estimated as follows: dppene (0.49) > dppm (0.43) > dppe (0.28). A. B. P. Lever, *Inorg. Chem.*, **29**, 1271 (1990).

60 a) M. Akita, N. Shirasawa, S. Hikichi, and Y. Moro-oka, *Chem. Commun.*, 973 (1998). b) N. Shirasawa, M. Akita, S. Hikichi, and Y. Moro-oka, *Chem. Commun.*, **1999**, 417. c) N. Shirasawa, T. T. Nguyet, S. Hikichi, Y. Moro-oka, and M. Akita, *Organometallics*, **20**, 3582 (2001).

61 A. Yamamoto, "Organotransition Metal Chemistry," Wiley-Interscience, New York, (1986). J. P. Collman, L. S. Hegedus, J. R. Norton, and R. G. Finke, "Principles and Applications of Organotransition Metal Chemistry," 2nd ed, University Science Books, Mill Valley (1987). R. H. Crabtree, "The Organometallic Chemistry of the Transition Metals," 3rd ed, Wiley-Interscience, New York (2001). B. Cornils and W. Herrmann, "Applied Homogeneous Catalysis with Organometallic Compounds (2 Vols.)," VCH, Oxford (1996). E. W. Abel, F. G. A. Stone, and G. Wilkinson, "Comprehensive Organometallic Chemistry II," Pergamon, Oxford (1995).

62 a) R. J. Morris and G. S. Gilorami, *Organometallics*, **8**, 1478 (1989). b) See also refs cited in Ref. 60c.

63 H. Lehmkuhl, J. Näser, G. Mehler, T. Keil, F. Danowski, R. Benn, R. Mynott, G. Schroth, B. Gabor, C. Krüger, and P. Betz, *Chem. Ber.*, **124**, 441 (1991).

64 Stable square-planar d^8 metal complexes with an additional ligand are known. M. Kujime, S. Hikichi, and M. Akita, *Organometallics*, **20**, 4049 (2001) and Refs. cited therein.

65 a) G. N. La Mar, W. D. W. Horrocks, Jr., and R. H. Holm, "NMR of paramagnetic molecules: principles and applications," Academic Press, New York, (1973). b) A. B. P. Lever, *Coord. Chem. Rev.*, **150**, 1 (1996).

66 a) D. F. Shriver, and P. W. Atkins, "Inorganic Chemistry," 3rd ed, Oxford University Press, Oxford (1999). b) F. A. Cotton, G. Wilkinson, C. A. Murillo, and M. Bochmann, "Advanced Inorganic Chemistry," 6th ed, Wiley-Interscience, New York (1999).

67 **35**: a) J. L. Kisko, T. Hascall, and G. Parkin, *J. Am. Chem. Soc.*, **120**, 10561 (1998). **36**: b) J. D. Jewson, L. M. Liable-Sands, G. P. A. Yap, A. L. Rheingold, and K. H. Theopold, *Organometallics*, **18**, 300 (1999). **37**: c) P. J. Schebler, B. S. Mandimutsira, C. G. Riordan, L. M. Liable-Sands, C. D. Incarvito, and A. L. Rheingold, *J. Am. Chem. Soc.*, **123**, 331 (2001).

68 F. A. Cotton, B. A. Frenz, and A. Shaver, *Inorg. Chim. Acta*, **7**, 161 (1973).

69 J. L. Detrich, R. Konecny, W. M. Vetter, D. Doren, A. L. Rheingold, and K. H. Theopold, *J. Am. Chem. Soc.*, **118**, 1703 (1996).

70 a) S. D. Ittel, L. K. Johnson, and M. Brookhart, *Chem. Rev.*, **100**, 1169 (2000). b) G. J. P. Britovsek, V. Gibson, and D. F. Wass, *Angew. Chem., Int. Ed.*, **38**, 428 (1999).

71 K. Uehara, S. Hikichi and M. Akita, *Organometallics*, **20**, 5002 (2001).

72 O. M. Abu Salah, and M. I. Bruce, *Aust. J. Chem.*, **30**, 2291 (1977). CpMo(H)$_2$CuTp reported therein might be supported only by the dative Mo→Cu bond but the interaction mode of the hydride ligands (η^1 or μ) has been left unclarified.

73 Bimetallic complexes with bridging ligands or coordinatively saturated Tp^{R}ML$_n$-type fragments: a) M. D. Curtis, K.-B. Shiu, W. M. Butler, and J. C. Huffman, *J. Am. Chem. Soc.*, **108**, 3335 (1986). b) Y.-Y. Liu, A. Mar, S. J. Rettig, A. Storr, and J. Trotter, *Can. J. Chem.*, **66**, 1997 (1988). c) M. M. de V. Steyn, E. Singleton, S. Hietkamp, and D. C. Liles, *J. Chem. Soc., Dalton Trans.*, **1990**, 2991. d) K. B. Shiu, W.-N. Guo, S.-M. Peng, and M.-C. Cheng, *Inorg. Chem.*, **33**, 3010 (1994).

74 A few Tp^{R}M-M′L$_n$-type dimetallic complexes, where M and M′ are a main group metal and a transition metal, respectively, are known. D. L. Reger, S. S. Mason, A. L. Rheingold, B. S. Haggarty, and F. P. Arnold, *Organometallics*, **13**, 5049 (1994). D. L. Reger, D. G. Garza, A. L. Rheingold, and G. P. A. Yap, *Organometallics*, **17**, 3624 (1998).

75 a) L. H. Gade, *Angew. Chem., Int. Ed.*, **39**, 2659 (2000).

For early-late heterobimetallics, see for example b) N. Wheatley and P. Kalck, *Chem. Rev.*, **99**, 3379 (1999).

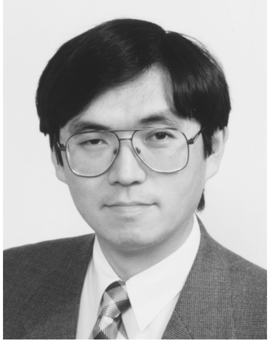
76 a) G. Fachinetti, G. Fochi, T. Funaioli, and P. F. Zanazzi, *Angew. Chem., Int. Ed.*, **26**, 680 (1987). b) G. N. Harakas and B. R. Whittlesey, *J. Am. Chem. Soc.*, **118**, 4219 (1996). c) L. H. Gade, *Angew. Chem., Int. Ed.*, **35**, 2089 (1996), and Refs. cited therein.

77 K. Uehara, S. Hikichi and M. Akita, unpublished results.

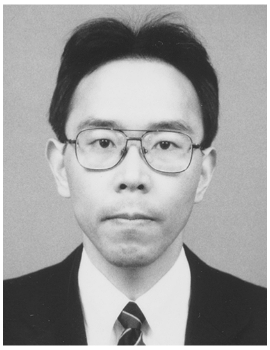
78 W. B. Bang and G. B. Carpenter, *Acta Crystallogr.*, **17**, 742 (1964).

79 a) I. Nagy-Gergely, G. Szalontai, F. Ungvary, L. Marko, M. Moret, A. Sironi, C. Zucchi, A. Sisak, C. M. Tschoerner, A. Martinelli, A. Sorkau, and G. Palyi, *Organometallics*, **16**, 2740 (1997). b) Averaged values. c) PPN salt. d) $[Rh(CN\text{-}o\text{-xylyl})_4]$-$[Co(CO)_4]$: I. Ojima, N. Clos, J. Donovan, and P. Ingallina, *Organometallics*, **10**, 3211 (1991).

80 A. Roberts, W. C. Mercer, S. M. Zahurak, G. L. Geoffroy, C. W. DeBrosse, W. E. Cass, and C. G. Pierpont, *J. Am. Chem. Soc.*, **104**, 910 (1982). P. S. Bearman, A. K. Smith, N. C. Tong, and R. Whyman, *Chem. Commun.*, **1996**, 2061. M. Schubart, G. Mitchell, L. H. Gade, T. Kottke, I. J. Scowen, and M. Macpartlin, *Chem. Commun.*, **1999**, 233.



Munetaka Akita was born in 1957 in Fukuoka, Japan. He graduated from Kyoto University with B. Eng. (1979) and M. Eng. degrees (1981) under the supervision of Professor Makoto Kumada. Having completed his Ph. D. work with Professor Akira Nakamura of Osaka University in 1984, he worked with Professor Yoshihiko Moro-oka at the Research Laboratory of Resources Utilization (now the Chemical Resources Laboratory), Tokyo Institute of Technology, as a research associate and later as an associate professor. He was promoted to be professor of a new division established in the same institution in April 2002. During 1989–1990 he worked with Professor J. R. Shapley at the University of Illinois as a postdoctoral fellow. He is currently interested in inorganic chemistry related to catalytic processes, in particular, the chemistry of Tp^R-metal complexes and polycarbon metal complexes.



Shiro Hikichi was born in Tokyo in 1966. He studied bioinorganic chemistry and coordination chemistry to receive his Ph. D. from Tokyo Institute of Technology in 1995. He continued his research at the same institute as a JSPS fellow and then at Massachusetts Institute of Technology as a postdoctoral researcher with Prof. Stephen J. Lippard. In 1996, he was invited to the Chemical Resources Laboratory of his alma mater as a research associate. He received the 2000 Progress Award for Young Chemist from the Chemical Society of Japan. Since October 2001 he has been a lecturer at the Department of Applied Chemistry, the Graduate School of Engineering, the University of Tokyo.