Selective Synthesis, Characterization, and Configurational Flexibility of the Coordinatively Unsaturated Metal Center of Half-Sandwich Type Complexes with the Less-Hindered Hydrotris(3, 5-dimethyl-4-X-1-pyrazolyl)borate Ligands [$\mathrm{Tp}^{\mathrm{Me_2,X}}\mathrm{M}^{\mathrm{II}}(\kappa^2\text{-}O,O'\text{-L})$] (M = Ni, Co; L = NO_3, OAc; X = Me, H, Br)

Shiro Hikichi,[*,#] **Yasuyuki Sasakura, Michito Yoshizawa, Yoshiko Ohzu, Yoshihiko Moro-oka, and Munetaka Akita**[*]

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

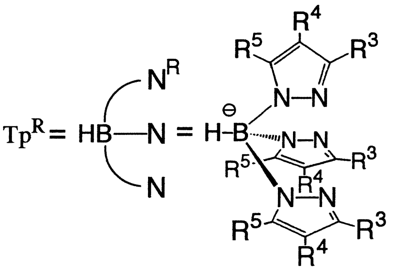
(Received September 7, 2001)

The selective synthesis of half-sandwich type complexes of Ni(II) and Co(II) with the less-hindered hydrotris(3,5-dimethyl-4-X-1-pyrazolyl)borate [X = Me ($\mathrm{Tp}^{\mathrm{Me_3}}$; **a** series), H ($\mathrm{Tp}^{\mathrm{Me_2}}$; **b** series), and Br ($\mathrm{Tp}^{\mathrm{Me_2,Br}}$; **c** series)] ligands, [$\mathrm{Tp}^{\mathrm{Me_2,X}}\mathrm{M}^{\mathrm{II}}(\kappa^2\text{-}O,O'\text{-L})$] [L = NO_3 (**2**), OAc (**3**)], has been achieved by dropwise addition of a THF solution of $\mathrm{NaTp}^{\mathrm{Me_2,X}}$ to an excess amount of ML_2 dissolved in MeOH. The solid state structures of the nitrato complexes **2** have been characterized by X-ray crystallography as their solvated form, **2·solv.** (solv. = MeCN, MeOH), in which the metal centers have the six-coordinated octahedral geometry. Solvates are readily dissociated from the metal center upon dissolution in non-coordinationg solvents, such as CH_2Cl_2 and toluene, as well as drying of a solid sample to give the non-solvated five-coordinated species **2**. The crystal structure of the non-solvated $\mathrm{Tp}^{\mathrm{Me_2}}$Ni derivative $\mathbf{3b^{Ni}}$ consists of a highly distorted trigonal bipyramidal nickel center.

Hydrotris(1-pyrazolyl)borates, Tp^{R} (R denotes substituents on the pyrazolyl groups; Chart 1), have been extensively utilized to study coordination chemistry, because Tp^{R} forms a relatively stable metal-ligand fragment due to an electrostatic interaction as well as a chelate effect arising from their mononegative, multidentate properties. Another advantage of Tp^{R} is ease of controlling the properties of metal complexes (coordination environment and reactivity of metal centers, good solubility in organic solvents, facile crystallization, etc.) by introducing various substituents onto the pyrazolyl rings.[1] In particular, sterically hindered Tp^{R} ligands, which contain relatively bulky alkyl substituents, such as isopropyl (= *i*Pr) and *t*-butyl (= *t*Bu) groups at the 3-position of the pyrazolyl rings, have led to the isolation and structural determination of several attractive compounds, such as thermally unstable dioxygen complexes and highly coordinatively unsaturated alkyl complexes.[2–6] Although a wide variety of Tp^{R} has been developed, a prototype of hydrotris(1-pyrazolyl)borate, $\mathrm{Tp}^{\mathrm{H_2}}$, and its methylated analogue, $\mathrm{Tp}^{\mathrm{Me_2}}$, have been used most extensively because of the ease of their availability. In the chemistry of such less-hindered Tp^{R} systems, however, investigations of first-row late transition metals are less than those of second- and third-row metals because the less hindered Tp^{R} readily yields coordinatively saturated ferrocene-type sandwich complexes of first-row divalent metals, [$\mathrm{M}^{\mathrm{II}}(\mathrm{Tp}^{\mathrm{R}})_2$] (i.e. ligand : metal = 2 : 1),[7] which are usually inert toward any further ligand displacement reaction.[1]

Previously, we reported on the synthesis of halo, nitrato and carboxylato complexes of divalent late transition metals with the $\mathrm{Tp}^{i\mathrm{Pr_2}}$ and $\mathrm{Tp}^{t\mathrm{Bu},i\mathrm{Pr}}$ ligands, [$\mathrm{Tp}^{\mathrm{R}}\mathrm{M}^{\mathrm{II}}\mathrm{L}$] (L denotes mononegative ligand), regarded as "half-sandwich type (i. e. ligand : metal = 1 : 1)" complexes. In such a highly sterically demanding Tp^{R} system, mixing a methanol solution of the appropriate metal salt (= ML_2) and a THF solution of $\mathrm{KTp}^{\mathrm{R}}$ all at once resulted in a selective displacement of one of the two anions of ML_2 with the mononegative Tp^{R} ligand to give the desired half-sandwich type complexes.[2,3,8,9] In contrast to the highly hindered ligands (i. e. $\mathrm{Tp}^{i\mathrm{Pr_2}}$ and $\mathrm{Tp}^{t\mathrm{Bu},i\mathrm{Pr}}$), less-hindered hydrotris(3, 5-dimethyl-4-X-1-pyrazolyl)borates, $\mathrm{Tp}^{\mathrm{Me_2,X}}$ [$\mathrm{Tp}^{\mathrm{Me_3}}$: X = Me (**a** series), $\mathrm{Tp}^{\mathrm{Me_2}}$: X = H (**b** series), $\mathrm{Tp}^{\mathrm{Me_2,Br}}$ (**c** series)], readily yields inert sandwich complexes, [$\mathrm{M}^{\mathrm{II}}(\mathrm{Tp}^{\mathrm{Me_2,X}})_2$] (**1**),[7a] under the same reaction conditions. It should be noted that the $\mathrm{Tp}^{\mathrm{Me_2,X}}$ ligands contain methyl groups that are much more resistant to oxidative ligand deformation (H-abstraction from the alkyl substituent) compared to the isopropyl groups in $\mathrm{Tp}^{i\mathrm{Pr_2}}$; such a property results in stabilization of the reactive dinuclear high-valent metal-bis(μ-oxo) species, [$\{\mathrm{Tp}^{\mathrm{Me_2,X}}\mathrm{M}^{\mathrm{III}}\}_2(\mu\text{-O})_2$] (M = Ni, Co).[10] Herein we report on the selective synthesis and characterization of the half-sandwich type complexes with the less hindered $\mathrm{Tp}^{\mathrm{Me_2,X}}$ ligands, [$\mathrm{Tp}^{\mathrm{Me_2,X}}\mathrm{M}^{\mathrm{II}}(\kappa^2\text{-}O,O'\text{-L})$] (M = Ni, Co; L = NO_3 (**2**), OAc (**3**)), which are starting materials of the bimetallic bis(μ-oxo) complexes.[10]

[#] Present address: Department of Applied Chemistry, Graduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656



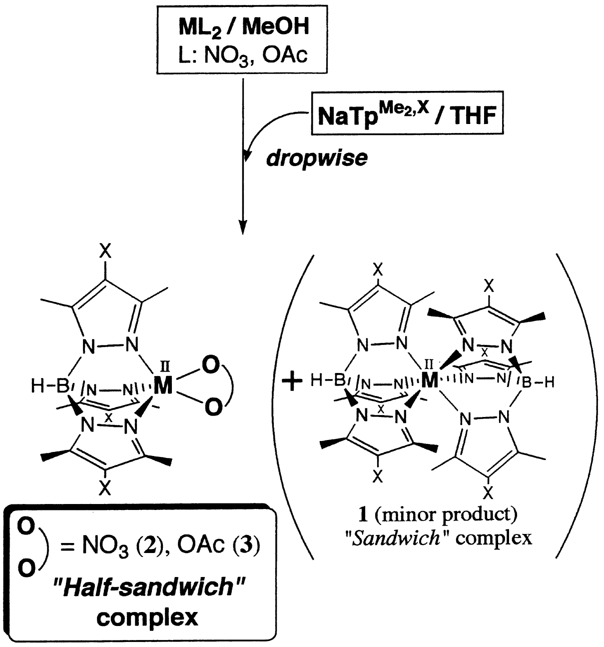
	R^3	R^4	R^5
Tp^{Me3} (**a** series)	Me	Me	Me
Tp^{Me2} (**b** series)	Me	H	Me
$Tp^{Me2,Br}$ (**c** series)	Me	Br	Me
Tp^{iPr2}	iPr	H	iPr
Tp^{H2}	H	H	H
Tp^{tBu}	tBu	H	H
$Tp^{tBu,iPr}$	tBu	H	iPr
$Tp^{CF_3,Me}$	CF_3	H	Me

Chart 1. Hydrotris(pyrazolyl)borate ligands Tp^R (appearing in this paper).

Results and Discussion

Synthesis of the κ^2-Chelating NO_3 and OAc Complexes. In the case of the above-mentioned highly hindered ligand systems, the bulky substituents on Tp^R (= isopropyl or *t*-butyl groups surrounding the metal center) prevent the coupling of $[Tp^RM^{II}L]$ with a second equivalent of the ligand leading to the undesired $[M(Tp^R)_2]$. In other words, $[Tp^RM^{II}L]$ is stabilized kinetically. In this study, we designed another synthetic method for a half-sandwich complex with the less-hindered $Tp^{Me_2,X}$ based on the kinetic stabilization effect; *a THF solution of $NaTp^{Me_2,X}$ was added dropwise to a MeOH solution of an excess amount (1.1 – 1.5 equivalent) of ML_2.* In this procedure, the amount of $NaTp^{Me_2,X}$ is not sufficient for the formation of the 1:2 adducts (sandwich complexes). In addition, the resulting half-sandwich complexes, **2** and **3**, containing the κ^2-ligand (L) should be less reactive toward a second equivalent of the $Tp^{Me_2,X}$ anion than the $[Tp^{Me_2,X}M(\kappa^1\text{-L})]$ (L = halide), because the bidentate ligand (κ^2-L) produces a five-coordinated metal center which is closer to the coordinatively saturated (= six-coordinated octahedron) situation compared to the monodentate ligand (κ^1-L) system.

As we expected, the desired nitrato (**2**) and acetato (**3**) complexes were successfully obtained as major products (Scheme 1). Although the formation of the ferrocene-type sandwich complexes **1** could not be avoided perfectly, the much lower solubility of **1** in MeCN allowed purification of the product by extraction with MeCN. The solvent adducts of the nitrato complexes, $[Tp^{Me_3}M^{II}(\kappa^2\text{-}O,O'\text{-}NO_3)(MeCN)]$ [M = Ni (**$2a^{Ni}$(MeCN)**), Co (**$2a^{Co}$(MeCN)**)] and $[Tp^{Me_2}Co^{II}(\kappa^2\text{-}O,O'\text{-}NO_3)(MeOH)]$ (**$2b^{Co}$(MeOH)**), and the non-solvated acetatonickel complex, $[Tp^{Me_2}Ni^{II}(\kappa^2\text{-}O,O'\text{-}OAc)]$ (**$3b^{Ni}$**) were characterized by X-ray crystallography as well as spectroscopy (elemental analysis, IR, UV-vis, ^1H NMR, mass). To date, structurally characterized half-sandwich complexes of Co(II) and Ni(II) with the less hindered Tp^{H_2} and Tp^{Me_2} are still rare.[11,12] It should be noted that the functionalization of **2** and **3** is much more facile than that of **1**. For example, the bimetallic bis(μ-hydroxo) complexes, $[\{Tp^{Me_3}M^{II}\}_2(\mu\text{-}OH)_2]$,[10] could not be obtained from **1a** but from **2a** and **3a** by base hydrolysis. In addition, our established synthetic method can be applied to the synthesis of half-sandwich complexes with mononegative tripodal ligands other than Tp^R, such as Kläui's ligand, $\kappa^3\text{-}O,O',O''\text{-}\{(\eta^5\text{-}C_5H_5)Co[P(=O)(OR)_2]_3\}^-$, and our developed methylbis(1-methylimidazol-2-yl)(3-R-pyrazol-1-ly)borate, $\kappa^3\text{-}N,N',N''\text{-}[MeB(Im^{N\text{-}Me})_2(Pz^{3\text{-}R})]^-$ (Chart 2).[13,14]



Scheme 1.

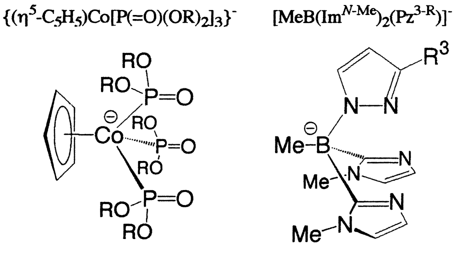


Chart 2.

Characterization of Nitrato Complexes 2. (a) X-ray Crystallography. Single crystals of the nitrato complexes with Tp^{Me_3}, **$2a^{Ni}$(MeCN)** and **$2a^{Co}$(MeCN)**, could be obtained from MeCN solutions. X-ray crystallography revealed that the overall structures (Fig. 1) and the unit cell and structural parameters of the Ni and Co derivatives are almost identical (Tables 1 and 3). In addition, the molecular structures of **2a(MeCN)** are very similar to that of the nitratocobalt complex with a fluorinated Tp^R ligand, $[Tp^{CF_3,Me}Co^{II}(\kappa^2\text{-}O,O'\text{-}NO_3)(MeCN)]$, reported by Gorun et al.[15] The metal centers are supported by the $\kappa^3\text{-}Tp^{Me_3}$, $\kappa^2\text{-}NO_3$ and MeCN ligands forming an octahedral geometry. One of the three pyrazolyl

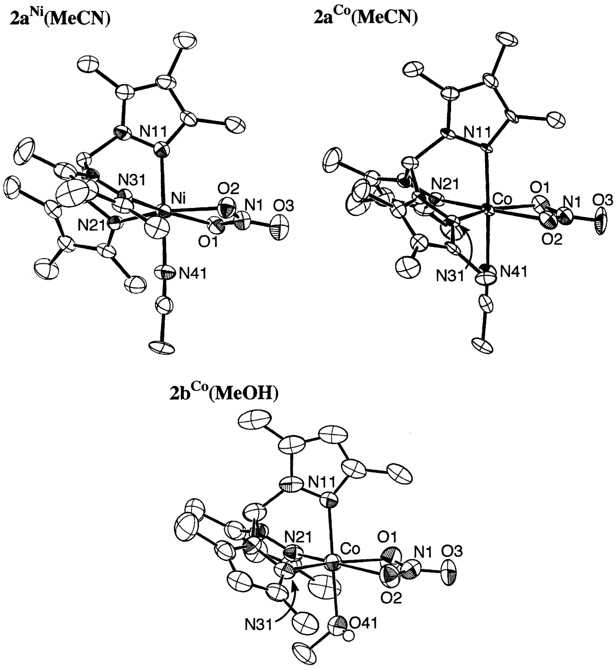
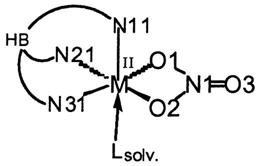

$2a^{Ni}$(MeCN) **$2a^{Co}$(MeCN)** **$2b^{Co}$(MeOH)**

Fig. 1. Molecular structures of the nitrato complexes **$2a^{Ni}$(MeCN)**, **$2a^{Co}$(MeCN)**, and **$2b^{Co}$(MeOH)** drawn at 50% probability level. All hydrogen atoms except that attached on the oxygen atom of MeOH in **$2b^{Co}$(MeOH)** are omitted for clarity.

groups of Tp^{Me_3} (N11) and the acetonitrile solvate (N41) serve as the axial ligands judging from the almost linear N11–M–N41 linkage and the slightly elongated M–N11 and M–N41 lengths compared to the remaining M–$N_{pyrazolyl}$ and M–O lengths are due to the Jahn–Taller distortion. The κ^2-NO_3 ligand occupies the equatorial position with almost the same M–O distances, in a manner so-called symmetrical bidentate mode. In contrast, a different coordination mode of the NO_3 ligand has been observed for the previously reported non-solvated five-coordinated nitrato complex of Co with Tp^{tBu} (= hydrotris(3-*t*-butyl-1-pyrazolyl)borate), $[Tp^{tBu}Co^{II}(\kappa^2\text{-}O,O'\text{-}NO_3)]$. As indicated in Chart 3, the two Co–O distances are not identical (i. e. unsymmetrical bidentate) and the geometry of the Co center is a highly distorted trigonal bipyramid, rather than a square pyramid, although the corresponding Ni derivative, $[Tp^{tBu}Ni^{II}(\kappa^2\text{-}O,O'\text{-}NO_3)]$, consists of a square-pyramidal Ni center supported by the symmetrically bidentate NO_3 ligand.[16]

Table 1. Selected Bond Lengths (Å) and Angles (°) of the Nitrato Complexes $[Tp^{Me_2,X}M^{II}\text{-}(\kappa^2\text{-}O,O'\text{-}NO_3)(\text{solv.})]$



Complex	**$2a^{Ni}$(MeCN)**	**$2a^{Co}$(MeCN)**	**$2b^{Co}$(MeOH)**
$Tp^{Me_2,X}$(X):M	Tp^{Me_3}(Me):Ni	Tp^{Me_3}(Me):Co	Tp^{Me_2}(H):Co
solv. (donor atom)	MeCN (N)	MeCN (N)	MeOH (O)
	Bond Lengths (Å)		
M–O1	2.157(2)	2.191(3)	2.160(8)
M–O2	2.122(2)	2.159(3)	2.222(6)
M–N11	2.087(2)	2.120(3)	2.103(8)
M–N21	2.046(2)	2.079(3)	2.056(7)
M–N31	2.032(2)	2.068(3)	2.06(1)
M–$L_{solv.}$	2.101(2)	2.148(4)	2.119(9)
O1–N1	1.274(3)	1.275(4)	1.27(1)
O2–N1	1.273(3)	1.266(4)	1.25(1)
O3–N1	1.221(4)	1.220(6)	1.23(1)
	Bond Angles (deg)		
O1–M–O2	60.49(6)	59.47(9)	58.3(3)
O1–M–N11	95.51(7)	96.3(1)	95.1(3)
O1–M–N21	105.54(7)	107.0(1)	101.7(3)
O1–M–N31	161.35(7)	161.0(1)	166.6(3)
O1–M–$L_{solv.}$	84.88(8)	84.7(1)	84.6(3)
O2–M–N11	94.97(8)	95.7(1)	100.1(3)
O2–M–N21	165.88(6)	166.4(1)	159.1(4)
O2–M–N31	101.08(7)	101.7(1)	108.4(3)
O2–M–$L_{solv.}$	86.63(8)	86.3(1)	79.3(3)
N11–M–N21	88.13(8)	86.8(1)	86.7(3)
N11–M–N31	88.55(7)	87.4(1)	88.0(3)
N11–M–$L_{solv.}$	178.34(8)	178.0(1)	179.3(3)
N21–M–N31	92.75(7)	91.8(1)	91.5(3)
N21–M–$L_{solv.}$	90.21(8)	91.2(1)	93.9(3)
N31–M–$L_{solv.}$	91.59(8)	92.2(1)	92.2(4)
M–O1–N1	91.1(1)	91.2(2)	94.2(7)
M–O2–N1	92.6(1)	92.9(2)	91.7(5)
O1–N1–O2	115.6(2)	116.2(4)	115.8(8)
O1–N1–O3	122.5(2)	121.8(3)	122(1)
O2–N1–O3	121.9(2)	122.0(3)	123(1)

Single crystals of **$2b^{Co}$(MeOH)** suitable for X-ray analysis were also successfully obtained from a MeOH/hexane mixture (Fig. 1; bottom). The overall structure of this Tp^{Me_2}Co complex **$2b^{Co}$(MeOH)** is similar to that of the above-mentioned Tp^{Me_3} derivatives **2a(MeCN)**, where the Co center is supported by an octahedral N_3O_3 ligand donor set involving a MeOH solvate serving as an axial ligand. It is notable that the short O41–H26(MeOH)···O2 distance [O41···O2, 2.77(1) Å; O41···O1, 2.88(1) Å; O41–H26, 0.619 Å; H26···O2, 2.684 Å (the position of H26 was refined)] indicates the presence of an intramolecular hydrogen-bonding interaction. Such an interaction influences the coordination structure of the nitrate ligand; the difference in the two Co–$O_{nitrate}$ lengths [Co–O2, 2.222(6) Å; Co–O1, 2.160(8) Å; $\Delta_{Co\text{–}O}$ = 0.06 Å] is somewhat larger than those observed for **2a(MeCN)** (ca. 0.03Å). Moreover, an intermolecular hydrogen-bonding interaction between the alcoholic OH group and O3 in the NO_3 ligand was observed, as indicated in Fig. 2 [H26···O3, 2.260 Å]. Therefore, the coordination of the MeOH ligand seems to be stabilized by these hydrogen-bonding interactions. Actually, **$2b^{Co}$(MeOH)** survived an X-ray diffraction measurement at room temperature, although the MeOH solvate was lost by drying under a vacuum (see below).

(b) Solution Behavior. As we described above, the solvated NO_3 complexes have coordinatively saturated (i. e. six-coordinated) metal centers. However, the color of a solid sample of **2(solv.)** changed from blue to green in Ni (**2^{Ni}**) and from red to purple in Co (**2^{Co}**) complexes upon drying under a vacuum. Such behavior could be explained in terms of a loss of the

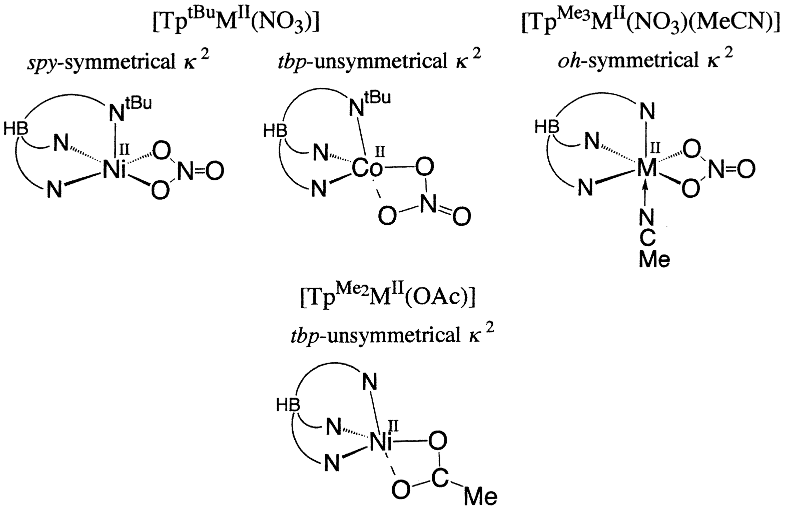


Chart 3.

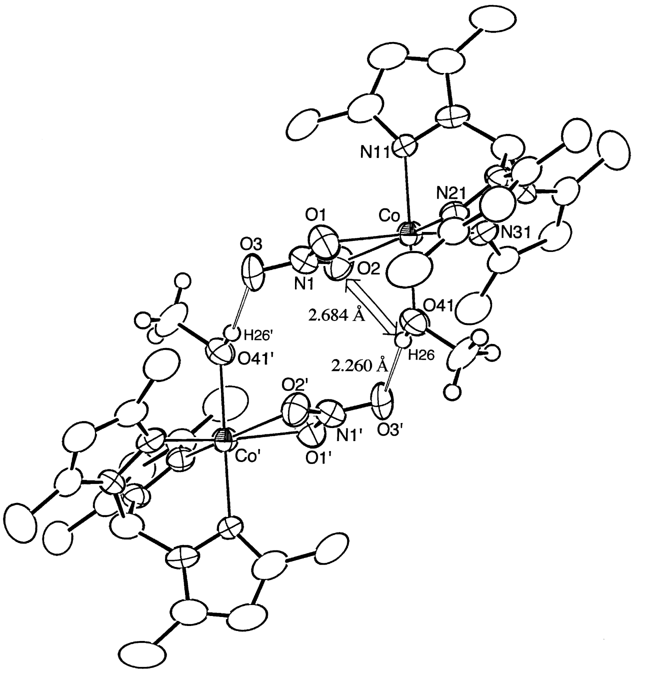


Fig. 2. Intramolecular hydrogen bonding interaction in **$2b^{Co}$(MeOH)**.

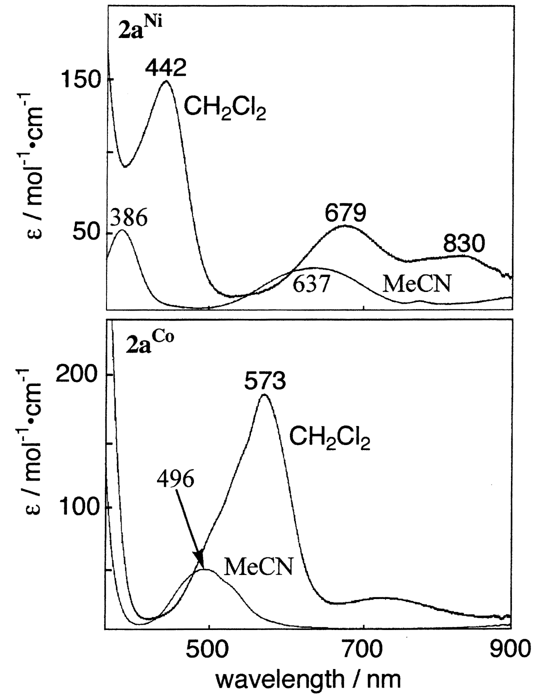


Fig. 3. UV-vis spectra of CH_2Cl_2 and MeCN solutions of **$2a^{Ni}$** (top) and **$2a^{Co}$** (bottom).

coordinated solvate to cause a change in the ligand-field splitting pattern. A solution of **2** showed color change consistent with the above-mentioned solid state behavior; the blue (Ni) and red (Co) color in MeCN solutions turned to green (Ni) and purple (Co) upon dissolution in non-coordinating solvents (i. e. CH_2Cl_2 and toluene), respectively.[17] Such a solvatochromic behavior was confirmed by UV-vis spectroscopy, as shown in Fig. 3.

The ^1H NMR spectra of **2a** also indicate a solvent-dependent change of the coordination structure. The spectral patterns are clearly different between the C_6D_6 and CD_3CN solutions. In both solutions, however, only a single set of the pz^{Me_3} signals (three methyl signals) was observed due to fast rotation of the Tp^R ligand. Although such a fluxional behavior of Tp^R is frequently observed for four- and five-coordinated first-row metal complexes,[8] the κ^3-binding Tp^R ligand in six-coordinated metal complexes is generally not fluxional. For instance, the Tp^{iPr_2} ligand of the acyldi(carbonyl)iron complex, $[Tp^{iPr_2}Fe^{II}(\eta^1\text{-}C(=O)Et)(CO)_2]$, with the octahedral iron center does not show the fluxional behavior, while that of the five-coordinated nickel-acyl-monocarbonyl complex, $[Tp^{iPr_2}Ni^{II}(\eta^1\text{-}C(=O)Et)(CO)]$, is fluxional.[6b,c] As indicated above, the blue (Ni) and red (Co) colors of the CD_3CN solutions of the nitrato complexes suggest that the coordination number of the metal centers is six, as found in the solid state structure (vide supra). We thus conclude that the weakly coordinated acetonitrile ligand is easily dissociated from the metal center to form a

Table 2. Selected Bond Lengths (Å) and Angles (°) of the Acetato Complex [Tp^{Me_2}Ni^{II}(κ^2-*O*,*O′*-OAc)] (**3b**^{Ni})

Bond lengths (Å)							
Ni–O1	2.014(3)	Ni–O2	2.131(4)	Ni–N11	2.031(3)	Ni–N21	1.996(3)
Ni–N31	1.994(3)	O1–C1	1.244(7)	O2–C1	1.188(6)		

Bond angles (deg)					
O1–Ni–O2	60.5(2)	O1–Ni–N11	101.7(2)	O1–Ni–N21	118.9(2)
O1–Ni–N31	146.5(2)	O2–Ni–N11	161.1(1)	O2–Ni–N21	103.1(1)
O2–Ni–N31	100.7(1)	N11–Ni–N21	91.0(1)	N11–Ni–N31	91.3(1)
N21–Ni–N31	91.2(1)	Ni–O1–C1	92.1(3)	Ni–O2–C1	88.1(3)
O1–C1–O2	118.7(4)				

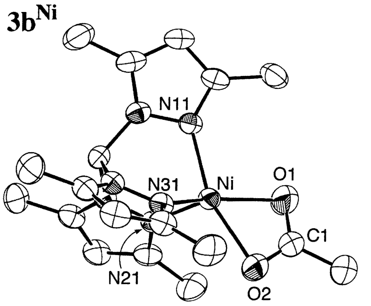


Fig. 4. ORTEP representation of the acetatonickel complex **3b**^{Ni} (50% probability level; all hydrogen atoms are omitted).

five-coordinated species, which undergoes the dynamic behavior of the Tp^R ligand.

Characterization of the Acetato Complexes 3. The acetato complexes **3** could also be isolated by recrystallization from MeCN solutions as blue (**3**^{Ni}**(MeCN)**) and red (**3**^{Co}**(MeCN)**) crystals. As observed for the above-mentioned nitrato complexes **2(solv.)**, the coordinated MeCN molecule was easily lost to give green (Ni) and purple (Co) compounds by vacuum drying; a spectroscopic analysis supported their formulation as the desired half-sandwich acetato complexes, [Tp^{Me_2,X}M^{II}(OAc)].

Finally, the molecular structure of the non-solvated acetatonickel complex **3b**^{Ni} was determined by X-ray crystallography, as represented in Fig. 4; the pertinent structural parameters are summarized in Table 2. Based on the O2–Ni–N21 angle [161.1(1)°] and the sum of the inter-ligand angles [O1–Ni–N21, 118.9(2)°; O1–Ni–N31, 146.5(2)°; N21–Ni–N31, 91.2(1)°: total = 356.6°], the geometry of the Ni center is best described as a highly distorted trigonal bipyramid (*tbp*) rather than a square pyramid (*spy*). Two Ni–O lengths are not identical; the distance from the nickel center to the axial O2 atom [2.131(4) Å] is longer than that to the equatorial O1 atom [2.014(3) Å], and the coordination fashion of the ligand is a so-called unsymmetrical bidentate. The dissimilar Ni–O lengths should be a result of incomplete delocalization of π electrons over the O–C–O linkage and, accordingly, the bond length of O2–C1 [1.188(6) Å] is shorter than that of O1–C1 [1.244(7) Å]. In contrast, a five-coordinated square-pyramidal Ni center supported by a symmetrical bidentate ligand is observed in the mononuclear nitrato and dinuclear μ-carbonato complexes, [Tp^{tBu}Ni^{II}(κ^2-NO$_3$)][16] and [{Tp^{iPr_2}Ni^{II}}$_2$(μ-κ^2:κ^2-CO$_3$)].[8] Moreover, the above-mentioned **2a**^{Ni}**(MeCN)** contains an octahedral Ni center with a symmetrical bidentate NO$_3$ (see Chart 3). Therefore, the cavity around the metal center formed by three alkyl substituents on Tp^R has a sufficient size to allow the various geometries of the metal center; also, the energy barrier for the structural change between spy and *tbp* is relatively small.

Conclusion

The half-sandwich complexes of Ni(II) and Co(II) with the less-hindered Tp^{Me_2,X} ligands, [Tp^{Me_2,X}M^{II}(κ^2-*O*,*O′*-L)] [L = NO$_3$ (**2**), OAc (**3**)], have been synthesized and characterized. The solid state structures of the nitrato complexes **2** have been revealed by X-ray crystallography as their solvated form, **2(solv.)** (solv. = MeCN, MeOH), in which the metal centers have the six-coordinated octahedral geometry. The coordinating solvent molecules are readily dissociated from the metal center in solutions as well as upon drying a solid sample to give the five-coordinated species. The trigonal bipyramidal nickel center of the acetato complex, [Tp^{Me_2}Ni^{II}(κ^2-*O*,*O′*-OAc)] (**3b**^{Ni}), indicates the configurational flexibility of the coordinatively unsaturated metal center with the chelating ligand.

Our developed synthetic method for [Tp^{Me_2,X}M^{II}(κ^2-L)] can be applied to half-sandwich complexes with ligands other than Tp^R. In order to reveal the ligand effects for the reactivity of the coordinatively unsaturated first-row late transition-metal compounds, systematic investigations on the synthesis and characterization of the half-sandwich complexes with the various Tp^R ligands and the other mononegative tripodal ligands are now under way.

Experimental

Instruments. IR measurements were carried out as KBr pellets using a JASCO FT/IR-5300 instrument. Electronic spectra were recorded on a Shimadzu UV-260 spectrometer or a JASCO V-570 spectrometer. NMR spectra were recorded on a Bruker AC-200 (^{1}H; 200 MHz) spectrometer. FD-Mass spectra were recorded on a Hitachi M-80.

Materials and Methods. All manipulations were performed under argon by standard Schlenk techniques. THF, Et$_2$O, hexane (Na–K alloy), toluene (Na), CH$_2$Cl$_2$ (P$_2$O$_5$), MeCN (CaH) were treated with appropriate drying agents, distilled, and stored under argon. The other reagents of the highest grade commercially available were used without further purification. The previously reported NaTp^{Me_2,X} were prepared by the described method.[18]

Synthesis and Characterization of the Complexes. [Tp^{Me_2,X}M^{II}(κ^2-*O*,*O′*-L)] [L = NO$_3$ (2) and OAc (3)]. As a typical example, the synthetic procedure for the nitratonickel complex **2a**^{Ni} is described. To a MeOH solution (20 mL) of

$Ni(NO_3)_2 \cdot 6H_2O$ (980 mg), a THF solution (30 mL) of $NaTp^{Me_3}$ (785 mg, 2.17 mmol) was added dropwise over 30 min from a dropping funnel. After the addition, the volatiles were removed by evaporation. The resulting solid was extracted with CH_2Cl_2 in order to remove the metal salts (unreacted $Ni(NO_3)_2$ and $NaTp^{Me_3}$). The resulting extract was evaporated and then extracted with MeCN to remove $[Ni^{II}(Tp^{Me_3})_2]$. The resulting MeCN filtrate was concentrated and refrigerated at −30 °C. The obtained blue crystalline solid was well dried under a vacuum to obtain the analytically pure complex as green powder (706 mg, 1.53 mmol, 71% yield). **$[Tp^{Me_3}Ni^{II}(NO_3)]$ ($2a^{Ni}$):** Anal. Calcd for $C_{18}H_{28}BN_7NiO_3$: C, 47.00; H, 6.14; N, 21.32%. Found: C, 46.59; H, 6.59; N, 21.66%. IR (ν/cm^{-1}): 2516 (BH). FD-MS (*m*/*z*): 459 (M^+). UV-vis (CH_2Cl_2, r. t., λ/nm, ε/M^{-1} cm^{-1}): 442 (150), 679 (60), 830 (40); (MeCN, r. t., nm, ε/M^{-1} cm^{-1}): 386(50), 637(30). ^{1}H NMR (C_6D_6, r. t.): δ_H −8.77, 0.04, 6.6 (9H×3, s×3, *Me*); (CD_3CN, r.t.): δ_H −8.63, −2.78, 6.42 (9H×3, s×3, *Me*), 2.24 (3H, s, *Me*CN).

The other half-sandwich complexes with $Tp^{Me_2,X}$ were prepared following this procedure. **$[Tp^{Me_3}Co^{II}(NO_3)]$ ($2a^{Co}$):** Yield: 908 mg, 1.97 mmol, 63% [based on 1.14×10^3 mg (3.15 mmol) of $NaTp^{Me_3}$]. Anal. Calcd for $C_{18}H_{28}BCoN_7O_3$: C, 46.98; H, 6.13; N, 21.30%. Found: C, 46.82; H, 6.13; N, 21.31%. IR (ν/cm^{-1}): 2524 (BH). FD-MS (*m*/*z*): 460 (M^+). UV-vis (CH_2Cl_2, r. t., λ/nm, ε/M^{-1} cm^{-1}): 573 (180), 719 (20); (MeCN, r. t., nm, ε/M^{-1} cm^{-1}): 496 (50). ^{1}H NMR (C_6D_6, r. t.): δ_H −29.86, 6.78, 32.68 (9H×3, s×3, *Me*); (CD_3CN, r. t.): δ_H −60.86, 3.00, 41.39 (9H×3, s×3, *Me*), 4.25 (3H, s, *Me*CN). **$[Tp^{Me_2}Co^{II}(NO_3)]$ ($2b^{Co}$):** Yield: 869 mg, 2.08 mmol, 46% [based on 1.46×10^3 mg (4.57 mmol) of $NaTp^{Me_2}$]. Anal. Calcd for $C_{15}H_{22}BCoN_7O_3$: C, 43.08; H, 5.30; N, 23.45%. Found: C, 43.62; H, 5.32; N, 24.07%. IR (ν/cm^{-1}): 2515 (BH). UV-vis (CH_2Cl_2, r. t., λ/nm, ε/M^{-1}cm^{-1}): 570 (60). **$[Tp^{Me_3}Ni^{II}(OAc)]$ ($3a^{Ni}$):** Yield: 1.00×10^3 mg, 2.19 mmol, 79% [based on 999 mg (2.76 mmol) of $NaTp^{Me_3}$]. Anal. Calcd for $C_{20}H_{31}BN_6NiO_2$: C, 52.56; H, 6.84; N, 18.39%. Found: C, 52.27; H, 6.92; N, 18.50%. IR (ν/cm^{-1}): 2520 (BH). FD-MS (*m*/*z*): 456 (M^+). UV-vis (CH_2Cl_2, r. t., λ/nm, ε/M^{-1}cm^{-1}): 424 (260), 682 (60), 846 (50). ^{1}H NMR (200 MHz, C_6D_6, r. t.): δ_H −8.7, 1.0, 6.6 (9H×3, s×3, *Me*), 86.4 (3H, s, *OAc*). **$[Tp^{Me_2}Ni^{II}(OAc)]$ ($3b^{Ni}$):** Yield: 697 mg, 1.68 mmol, 49% [based on 1.10×10^3 mg (3.45 mmol) of $NaTp^{Me_2}$]. Anal. Calcd for $C_{17}H_{25}BN_6NiO_2$: C, 49.21; H, 6.07; N, 20.26%. Found: C, 48.59; H, 5.99; N, 20.15%. IR (ν/cm^{-1}): 2513 (BH). UV-vis (CH_2Cl_2, r. t., λ/nm, ε/M^{-1}cm^{-1}): 419 (180), 680 (40). ^{1}H NMR (200 MHz, $CDCl_3$, r. t.): δ_H −10.7, −9.3 (9H×2, s×2, *Me*), 71.5 (3H, s, *pz-4H*), 86.7 (3H, s, *OAc*). **$[Tp^{Me_2,Br}Ni^{II}(OAc)]$ ($3c^{Ni}$):** Yield: 376 mg, 0.577 mmol, 62% [based on 515 mg (0.924 mmol) of $NaTp^{Me_2,Br}$]. Anal. Calcd for $C_{17}H_{22}BBr_3N_6NiO_2$: C, 31.34; H, 3.40; N, 12.90%. Found: C, 31.55; H, 3.29; N, 12.75%. IR (ν/cm^{-1}): 2530 (BH). UV-vis (CH_2Cl_2, r. t., λ/nm, ε/M^{-1}cm^{-1}): 413 (90), 676 (20), 847 (15). ^{1}H NMR (200 MHz, $CDCl_3$, r. t.): δ_H −9.6, −0.6 (9H×2, s×2, *Me*). **$[Tp^{Me_3}Co^{II}(OAc)]$ ($3a^{Co}$):** Yield: 743 mg, 1.62 mmol, 71% [based on 785 mg (2.17 mmol) of $NaTp^{Me_3}$]. Anal. Calcd for $C_{20}H_{31}BCoN_6O_2$: C, 52.54; H, 6.85; N, 18.38%. Found: C, 52.38; H, 6.81; N, 18.41%. IR (ν/cm^{-1}): 2523 (BH). FD-MS (*m*/*z*): 457 (M^+). UV-vis (CH_2Cl_2, r. t., λ/nm, ε/M^{-1}cm^{-1}): 574 (80). ^{1}H NMR (200 MHz, C_6D_6, r. t.): δ_H −44.4, 4.7, 37.1 (9H×3, s×3, *Me*). **$[Tp^{Me_2}Co^{II}(OAc)]$ ($3b^{Co}$):** Yield: 372 mg, 0.896 mmol, 73% [based on 392 mg (1.23 mmol) of $NaTp^{Me_2}$]. Anal. Calcd for $C_{17}H_{25}BCoN_6O_2$: C, 49.18; H, 6.07; N, 20.24%. Found: C, 49.35; H, 5.99; N, 20.12%. IR (ν/cm^{-1}): 2515 (BH). UV-vis (CH_2Cl_2, r. t., λ/nm, ε/M^{-1}cm^{-1}): 571 (90). ^{1}H NMR (200 MHz, $CDCl_3$, r. t.): δ_H −55.9, 37.9 (9H×2, s×2, *Me*), 58.0 (3H, s, *pz-4H*). **$[Tp^{Me_2,Br}Co^{II}(OAc)]$ ($3c^{Co}$):** Yield: 253 mg, 0.388 mmol, 49% [based on 443 mg (0.796 mmol) of $NaTp^{Me_2,Br}$]. Anal. Calcd for $C_{17}H_{22}BBr_3CoN_6O_2$: C, 31.32; H, 3.40; N, 12.89%. Found: C, 31.80; H, 3.06; N, 12.61%. IR (ν/cm^{-1}): 2538 (BH). UV-vis (CH_2Cl_2, r. t., λ/nm, ε/M^{-1}cm^{-1}): 557 (100). ^{1}H NMR (200 MHz, $CDCl_3$, r. t.): δ_H −56.4, 37.9 (9H×2, s×2, *Me*).

X-ray Crystallography. The conditions (solvent, temperature; under Ar unless otherwise stated) for crystallization were as follows: **$2a^{Ni}$(MeCN)**·2MeCN (MeCN, −30 °C), **$2a^{Co}$(MeCN)**·2MeCN (MeCN, −30 °C), **$2b^{Co}$(MeOH)** (hexane/acetone/MeOH, r. t., air), **$3b^{Ni}$** (hexane/acetone, r. t., air). The crystals were mounted on glass fibers.

Diffraction measurements of **$2a^{Ni}$(MeCN)**·2MeCN and **$2a^{Co}$(MeCN)**·2MeCN were made on a Rigaku RAXIS IV imaging plate area detector with Mo $K\alpha$ radiation (λ = 0.71069 Å). Indexing was performed from three oscillation images which were exposed for 5 min. The crystal-to-detector distance was 110mm. Data collection parameters were as follows: the oscillation range, 6°; number of oscillation images, 30; and exposed time, 40 min. The data collections were carried out at −60°C. Readout was performed with a pixel size of 100 μm × 100 μm. The data processing was performed on an IRIS Indy computer.

Diffraction measurements of **$2b^{Co}$(MeOH)** and **$3b^{Ni}$** were made on Rigaku AFC-6R (**$2b^{Co}$(MeOH)**) or AFC-5S (**$3b^{Ni}$**) automated four-circle diffractometers. A Mo X-ray source equipped with a graphite monochrometer (Mo $K\alpha$, λ = 0.710690 Å) was used. Automatic centering and least-squares routines were carried out for all of the compounds with 20 reflections of $20° < 2\theta < 25°$ to determine the cell parameters. The data collections were completed with a ω-2θ scan at room temperature.

Crystallographic data and the results of refinements are summarized in Table 3. A structure analysis was performed on an IRIS O2 computer using the teXsan structure-solving program package.[19] Neutral scattering factors were obtained from the standard source.[20] In the reduction of data, Lorentz and polarization corrections were made. The structures were solved by combimmimg the direct method (SHELXS-86) and Fourier synthesis (DIRDIF).[21,22] Least-squares refinements were carried out using SHELXL-97 linked to teXsan.[23] All of the non-hydrogen atoms were refined anisotropically. Riding refinements were applied to all of the methyl hydrogen [$U_{iso}(H) = 1.2U_{iso}(C)$], and the other hydrogen atoms (except for the alcoholic hydrogen atom in **$2b^{Co}$(MeOH)**) were fixed at the calculated positions. The position of the alcoholic hydrogen atom in **$2b^{Co}$(MeOH)** was refined. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-163518 (**$2a^{Ni}$(MeCN)**·2MeCN), CCDC-163519 (**$2a^{Co}$(MeCN)**·2MeCN), CCDC-163520 (**$2b^{Co}$(MeOH)**), and CCDC-163521 (**$3b^{Ni}$**). Copies of the data can be obtained free of charge by applying to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. The crystallographic data have also been deposited as Document No. 75022 at the Office of the Editor of *Bull. Chem. Soc. Jpn.*

This research was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology (Nos. 08102006, 11740370 and 11228201).

Table 3. Crystallographic Data of **2a$^{\mathrm{Ni}}$(MeCN)**·2MeCN, **2a$^{\mathrm{Co}}$(MeCN)**·2MeCN, **2b$^{\mathrm{Co}}$(MeOH)**, and **3b$^{\mathrm{Ni}}$**

Compound	**2a$^{\mathrm{Ni}}$(MeCN)**· 2MeCN	**2a$^{\mathrm{Co}}$(MeCN)**· 2MeCN	**2b$^{\mathrm{Co}}$(MeOH)**	**3b$^{\mathrm{Ni}}$**
Formula	$C_{24}H_{37}BN_{10}NiO_3$	$C_{24}H_{37}BCoN_{10}O_3$	$C_{16}H_{26}BcoN_7O_4$	$C_{17}H_{25}BN_6NiO_2$
Formula weight	583.13	583.36	450.17	414.93
Crystal system	triclinic	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$(#2)	$P\bar{1}$(#2)	$P\bar{1}$(#2)	$P2_1/a$(#14)
a/Å	12.0155(2)	12.013(2)	10.185(3)	18.942(3)
b/Å	12.0440(6)	12.037(2)	11.916(4)	7.796(2)
c/Å	12.0498(6)	12.058(2)	10.065(3)	13.941(3)
α/deg	64.769(2)	64.829(4)	103.09(3)	
β/deg	85.415(3)	85.768(6)	114.40(2)	104.15(1)
γ/deg	82.113(3)	82.361(6)	74.19(2)	
V/Å^3	1562.1(1)	1563.8(4)	1061.1(6)	1996.3(7)
Z	2	2	2	4
D_{calcd}/g cm^{-3}	1.240	1.258	1.409	1.381
μ(Mo $K\alpha$)/cm^{-1}	6.620	5.897	8.455	9.961
2θmax/deg	55.0	55.0	45.0	50.0
No. of unique reflections	6528	6440	2760	3518
No. of observed reflections ($I > 2.0\sigma(I)$)	5771	5920	1566	2722
No. of Parameters Refined	365	364	273	251
R1[a)]	0.0430	0.0767	0.0668	0.0521
wR2[b)]	0.1383	0.2298	0.2104	0.1556

a) $R1 = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$(for data with $I > 2.0\sigma(I)$)

b) $wR2 = \{\Sigma[w(F_o{}^2-F_c{}^2)]^2/\Sigma[w(F_o{}^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o{}^2) + (0.1000P)^2]$ where $P = (F_o{}^2 + 2F_c{}^2)/3$ (for all data).

References

1 a) S. Trofimenko, “Scorpionates—The Coordination Chemistry of Polypyrazolylborate Ligands,” Imperial College Press, London (1999). b) S. Torofimenko, *Chem. Rev.*, **93**, 943 (1993).

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

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

4 Our recent report of dioxygen complexes chemistry (except Co complex; Ref. 3) based on $\mathrm{Tp}^{i\mathrm{Pr}_2}$ and $\mathrm{Tp}^{t\mathrm{Bu},i\mathrm{Pr}}$ ligands. V: a) M. Kosugi, S. Hikichi, M. Akita, and Y. Moro-oka, *J. Chem. Soc., Dalton Trans.*, **1999**, 1369. Mn: b) 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. c) H. Komatsuzaki, M. Satoh, N. Sakamoto, S. Hikichi, M. Akita, and Y. Moro-oka, *Inorg. Chem.*, **37**, 6554 (1998). Fe: d) T. Ogihara, S. Hikichi, M. Akita, and Y. Moro-oka, *Inorg. Chem.*, **37**, 2614 (1998). e) T. Ogihara, S. Hikichi, M. Akita, T. Uchida, T. Kitagawa, and Y. Moro-oka, *Inorg. Chim. Acta*, **297**, 162 (2000). Ru: f) Y. Takahashi, S. Hikichi, M. Akita, and Y. Moro-oka, *Chem. Commun.*, **1999**, 1491. Rh: g) Y. Takahashi, M. Hashimoto, S. Hikichi, M. Akita, and Y. Moro-oka, *Angew. Chem., Int. Ed.*, **38**, 3074 (1999). Pd: h) M. Akita, T. Miyaji, S. Hikichi, and Y. Moro-oka, *Chem. Commun.*, **1998**, 1005. i) M. Akita, T. Miyaji, S. Hikichi, and Y. Moro-oka, *Chem. Lett.*, **1999**, 813. Review: j) M. Akita, S. Hikichi, and Y. Moro-oka, *J. Synth. Org. Chem.*, **57**, 619 (1999). k) S. Hikichi, M. Akita, and Y. Moro-oka, *Coord. Chem. Rev.*, **198**, 61 (2000).

5 Other dioxygen complexes with the hindered Tp^{R} ligands. Co: a) J. W. Egan, Jr., B. S. Haggerty, A. L. Rheingold, S. C. Sendlinger, and K. H. Theopold, *J. Am. Chem. Soc.*, **112**, 2445 (1990). b) O. M. Reinaud, and K. H. Theopold, *J. Am. Chem. Soc.*, **116**, 6979 (1994). c) O. M. Reinaud, G. P. A. Yap, A. L. Rheingold, and K. H. Theopold, *Angew. Chem., Int. Ed. Engl.*, **34**, 2051 (1995). Fe: d) K. Kim, and S. J. Lippard, *J. Am. Chem. Soc.*, **118**, 4914 (1996).

6 Hydrocarbyl complexes of Fe, Co, and Ni. a) M. Akita, N. Shirasawa, S. Hikichi, and Y. Moro-oka, *Chem. Commun.*, **1998**, 973. 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). d) J. D. Jewson, L. M. Liable-Sands, G. P. A. Yap, A. L. Rheingold, and K. H. Theopold, *Organometallics*, **18**, 300 (1999). e) J. L. Kisko, T. Hascall, and G. Parkin, *J. Am. Chem. Soc.*, **120**, 10561 (1998).

7 a) S. Trofimenko, *J. Am. Chem. Soc.*, **89**, 6288 (1967). b) P. Cecchi, G. Gioia Lobbia, F. Marchetti, G. Valle, and S. Calogero, *Polyhedron*, **13**, 2173 (1994).

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

9 A chloropalladium complex with $\mathrm{Tp}^{i\mathrm{Pr}_2}$ was also prepared accoding to the same procedure by us. M. Akita, T. Miyaji, N. Muroga, C. Mock-Knoblauch, W. Adam, S. Hikichi, and Y. Moro-oka, *Inorg. Chem.*, **39**, 2096 (2000).

10 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, M. Akita, and Y. Moro-oka, *Chem. Lett.*, **1999**, 979. c) S. Hikichi, M. Yoshizawa, Y. Sasakura, H. Komatsuzaki, Y. Moro-oka, and M. Akita, *Chem. Eur. J.*, **7**, 5011 (2001).

11 J. S. Thompson, T. Sorrell, T. J. Marks, and J. A. Ibers, *J. Am. Chem. Soc.*, **101**, 4193 (1979).

12 a) 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). b) E. Gutiérrez, S. A. Hudson, A.

Monge, M. C. Nicaso, M. Paneque, and C. Ruiz, *J. Organomet. Chem.*, **551**, 215 (1998). c) P. J. Desrochers, R. W. Cutts, P. K. Rice, M. L. Golden, J. B. Graham, T. M. Barclay, and A. W. Cordes, *Inorg. Chem.*, **38**, 5690 (1990). d) Y.-J. Sun, P. Cheng, S.-P. Yan, Z.-H. Jiang, D.-Z. Liao, and P.-W. Shen, *Inorg. Chem. Commun.*, **3**, 289 (2000).

13 a) M. Akita, D. Ma, S. Hikichi, and Y. Moro-oka, *J. Chem. Soc., Dalton Trans.*, **1999**, 987. b) D. Ma, S. Hikichi, M. Akita, and Y. Moro-oka, *J. Chem. Soc., Dalton Trans.*, **2000**, 1123.

14 a) K. Fujita, S. Hikichi, M. Akita, and Y. Moro-oka, *J. Chem. Soc., Dalton Trans.*, **2000**, 117. b) K. Fujita, S. Hikichi, M. Akita, and Y. Moro-oka, *J. Chem. Soc., Dalton Trans.*, **2000**, 1255.

15 S. M. Gorun, Z. Hu, R. T. Stibrany, and G. Carpenter, *Inorg. Chim. Acta*, **297**, 383 (2000).

16 A. Looney, R. Han, K. McNeill, and G. Parkin, *J. Am. Chem. Soc.*, **113**, 9707 (1991).

17 Similar spectral change was observed for $[\mathrm{Tp}^{t\mathrm{Bu}}\mathrm{Ni}^{\mathrm{II}}(\mathrm{NO}_3)]$. R. Han, A. Looney, K. McNeill, G. Parkin, A. L. Rheingold, and B. S. Haggerty, *J. Inorg. Biochem.*, **49**, 105 (1993).

18 a) A. Albinati, M. Bovens, H. Ruegger, and L. M. Venanzi, *Inorg. Chem.*, **36**, 5991 (1997). b) A. Wlodarczyk, R. M. Richardson, M. D. Ward, J. A. McCleverty, M. H. B. Hursthouse, and S. J. Coles, *Polyhedron*, **15**, 27 (1996).

19 “teXsan, ver. 1.11,” Rigaku Corporation, Tokyo (2000).

20 D. T. Cromer, and J. T. Waber, in “International Tables for X-ray Crystallography, Vol. IV,” ed by J. A. Ibers, and W. C. Hamilton, Kynoch Press, Birmingham (1974), Table 2.2A.

21 G. M. Sheldrick, “SHELXS-86,” University of Göttingen (1986).

22 P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smith, and C. Smykalla, “DIRDIF 92,” University of Nijmegen (1992).

23 G. M. Sheldrick, “SHELXL-97,” University of Göttingen (1997).