

Coordinatively unsaturated organometallic system based on Tp ligand: tetrahedral $\text{Tp}^{\text{R}}\text{M-R}'$ and $\text{Tp}^{\text{R}}\text{M-M}'\text{L}_n$ species

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Abstract

Chemistry of the highly coordinatively unsaturated, tetrahedral hydrocarbyl and dinuclear complexes bearing a hydrotris(pyrazolyl)borate (Tp^{R}) ligand, $\text{Tp}^{\text{R}}\text{M-R}'$ and $\text{Tp}^{\text{R}}\text{M-M}'\text{L}_n$, is reviewed. The organometallic Tp^{R} complexes are prepared by salt elimination between the corresponding halide and Grignard reagents or metalates and fully characterized by spectroscopic and crystallographic methods. Although the number of the valence electrons of the resultant species is much shorter than that expected for a coordinatively saturated species (for mononuclear species: 14–15e vs. 18e; for dinuclear species: 29–32e vs. 34e), they turn out to be thermally stable. In particular, the ethyl complexes $\text{Tp}^{\text{iPr}_2}\text{M-CH}_2\text{CH}_3$ ($\text{M} = \text{Fe}, \text{Co}$) are stable with respect to β -hydride elimination. The tetrahedral structures of the obtained organometallic species cause a small ligand field splitting of the frontier orbitals to lead to a high spin configuration, which leaves no vacant coordination site, and this should be the origin of the thermal stability of the electron deficient species. Upon interaction with donors they are incorporated into the organometallic system via switching of the spin state, and selective reactions dependent on the nature of the donor molecules are observed for the dinuclear complexes. Thus the high spin species can be regarded as masked forms of coordinatively unsaturated intermediates, which are regarded as key intermediates of organometallic transformations.

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Keywords: Hydrocarbyl; Xenophilic; Coordinatively unsaturated species; Hydrotris(pyrazolyl)borate; High spin

1. Introduction

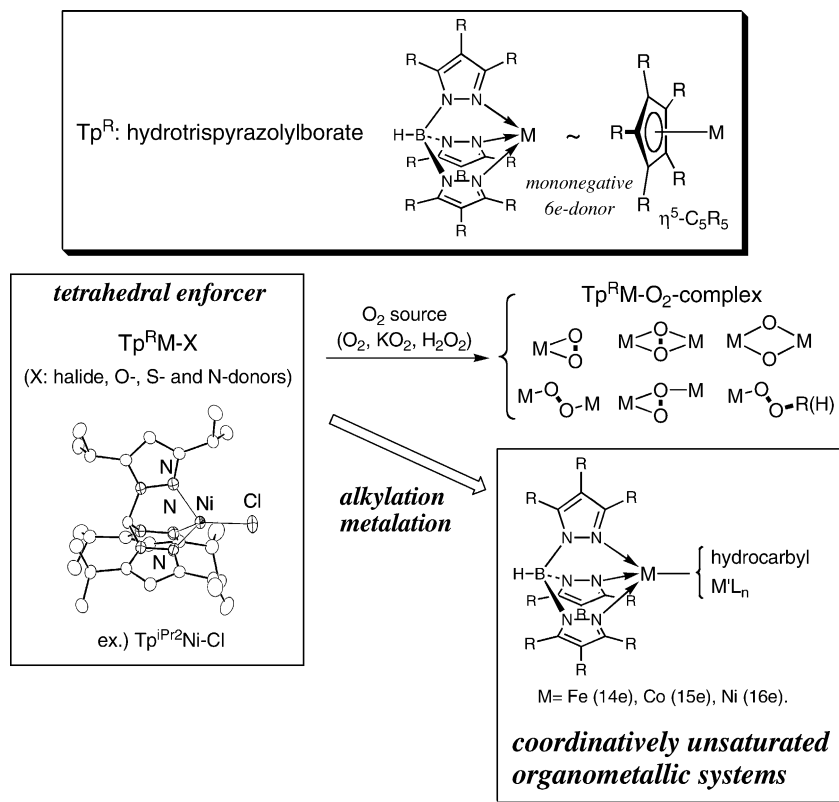
Coordinatively unsaturated species have been regarded as key intermediates of various stoichiometric and catalytic transformations mediated by organometallic species [1]. A substrate to be converted should be first incorporated into the coordination sphere of a coordinatively unsaturated transition metal intermediate and therefore it is essential for improvement of the efficiency of the transformations and development of new reactions to accumulate information on the

structure and reactivity of coordinatively unsaturated species. Although 16 valence electron species such as square-planar d^8 metal complexes and early transition metal complexes have been studied extensively, very few examples of *late transition metal hydrocarbyl complexes with less than 16 valence electrons* have been reported so far. In addition, almost all the previous examples of the late transition metal complexes contain bulky hydrocarbyl ligands without β -hydrogen atoms such as *ortho*-disubstituted aryl groups and $\text{CH}_2\text{ER}'_3$ groups ($\text{E} = \text{C}, \text{Si}$) [2], which kinetically stabilize the coordinatively unsaturated species by shielding the metal center.

We have enjoyed the rich chemistry based on hydrotris(pyrazolyl)borato ligand (Tp^{R} or scorpionate)

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Scheme 1.

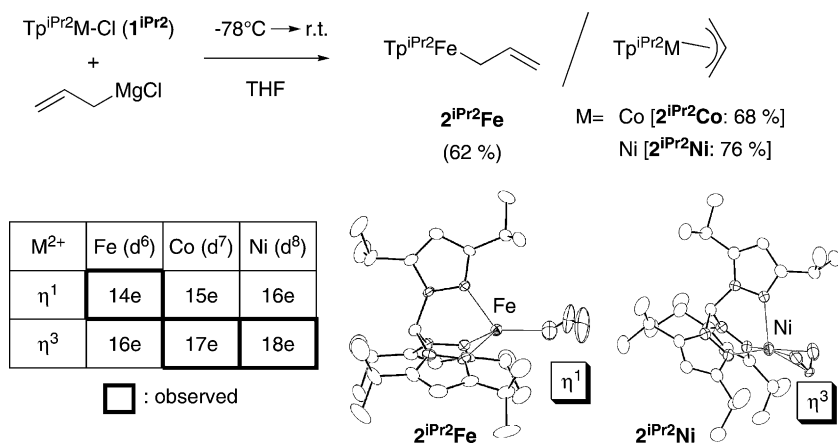
[3,4], in particular, systematic synthesis of dioxygen complexes of the first and second row metals (Scheme 1) [5]. The Tp^{R} ligand is usually coordinated to a transition metal center in a κ^3 -fashion and has been recognized as a ligand system isoelectronic with cyclopentadienyls ($\eta^5\text{-C}_5\text{R}_5$), which have been widely used in the studies of organometallic compounds, because both are mononegative 6e-donors. In addition to this feature, the Tp^{R} ligand is regarded as a “tetrahedral enforcer”, because it forms a variety of tetrahedral species, $(\kappa^3\text{-Tp}^{\text{R}})\text{M-X}$. The tetrahedral halo complexes $\text{Tp}^{\text{R}}\text{M-X}$ (X = Cl, Br, I) turn out to be versatile starting compounds for inorganic complexes including the dioxygen complexes. When we saw the tetrahedral structure of the halo precursors, we could not help alkylating them to obtain the hydrocarbyl complexes, $(\kappa^3\text{-Tp}^{\text{R}})\text{M-R}'$ (M = Fe, Co, Ni). We expected that, if such an attempt was successful, we might have an opportunity to study chemistry of highly coordinatively unsaturated hydrocarbyl complexes; the sum of valence electrons could be 14 (Fe), 15 (Co) and 16 (Ni).

Herein I wish to review the results of the study on the $(\kappa^3\text{-Tp}^{\text{R}})\text{M-R}'$ - and $(\kappa^3\text{-Tp}^{\text{R}})\text{M-M}'\text{L}_n$ -type highly coordinatively unsaturated organometallic systems, which have been obtained during last several years in our laboratory.

2. Hydrocarbyl complexes

2.1. Allyl complexes [6]

The first attempt that we made was allylation, because the allyl ligand was expected to donate more electrons to a coordinatively unsaturated metal center through η^3 -coordination. Treatment of the tetrahedral chloro precursors $\mathbf{1}^{\text{iPr}_2}$ with allyl Grignard reagent gave the corresponding allyl complexes $\mathbf{2}^{\text{iPr}_2}$ (Scheme 2). X-ray crystallography revealed the η^3 -coordination of the allyl ligand for the cobalt and nickel complexes $\mathbf{2}^{\text{iPr}_2}\text{Co, Ni}$ as we anticipated but, to our surprise, the η^1 -coordination was found for the iron complex $\mathbf{2}^{\text{iPr}_2}\text{Fe}$. Although the number of the d-electrons Fe^{II} (d^6) was smaller than those of cobalt and nickel (d^7 : Co^{II} ; d^8 : Ni^{II}), the allyliron complex $\mathbf{2}^{\text{iPr}_2}\text{Fe}$ adopted a η^1 -structure with 14 valence electrons (VEs) rather than a η^3 -structure with 16VEs, which was closer to a coordinatively saturated 18e configuration. The square-pyramidal structures for the cobalt and nickel complexes $\mathbf{2}^{\text{iPr}_2}\text{Co, Ni}$ with the η^3 -allyl and $\kappa^3\text{-Tp}^{\text{iPr}_2}$ ligands were also confirmed by spectroscopic methods and they were fluxional with respect to the exchange of the axial and basal pyrazolyl rings of the Tp^{R} ligand through a trigonal-bipyramidal intermediate as indicated by the single ^1H NMR signal set for the three pyrazolyl rings at



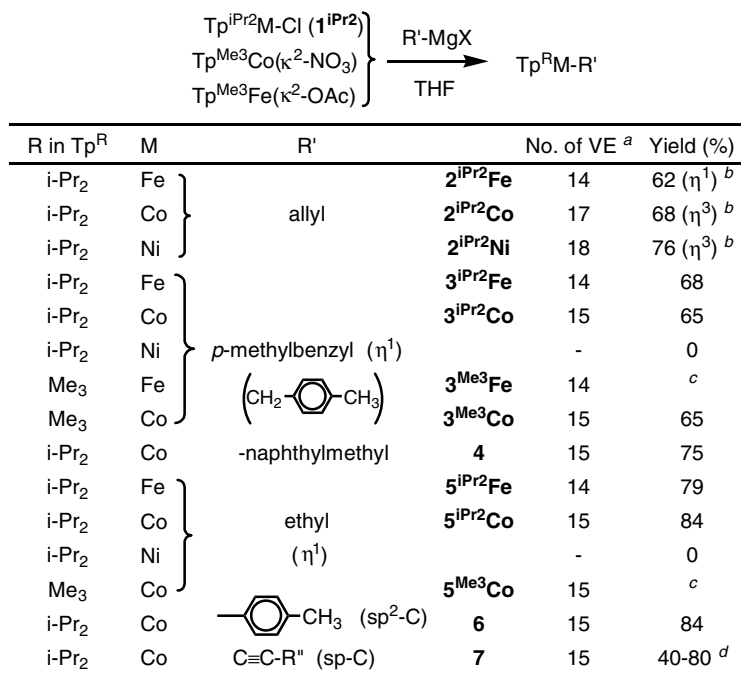
Scheme 2.

ambient temperature [7]. Thus the η¹-allyliron complex **2**^{iPr₂}Fe turned out to be a highly coordinatively unsaturated 14e species, whereas the η³-allyl-cobalt and -nickel complexes **2**^{iPr₂}Co, Ni were 17e and 18e species, respectively.

2.2. Hydrocarbyl complexes [8]

The successful synthesis and characterization of the 14e η¹-allyliron complex **2**^{iPr₂}Fe encouraged us to ex-

tend the synthesis to related hydrocarbyl complexes. As we expected, treatment of the chloro complexes of iron and cobalt **1**^{iPr₂}Fe, Co with various Grignard reagents readily afforded the corresponding hydrocarbyl complexes including the benzyl-type (**3**, **4**) and ethyl complexes (**5**) (Scheme 3) [9]. Attempted alkylation of the nickel complex **1**^{iPr₂}Ni gave a complicated mixture of products. In the case of ethylation of **1**^{iPr₂}Ni, because (1) alkylation under a CO atmosphere at -78 °C gave the propanoyl complex (κ³-Tp^{iPr₂})(OC)Ni-



^a number of valence electrons. ^b coord. mode of the allyl ligand.

^c not isolated in a pure form.

^d [Tp^{iPr₂}Co(μ-OH)]₂ + H-C≡C-R'' (R'' = COOMe, COMe, SiMe₃, H, Ph, *t*-Bu)

Scheme 3.

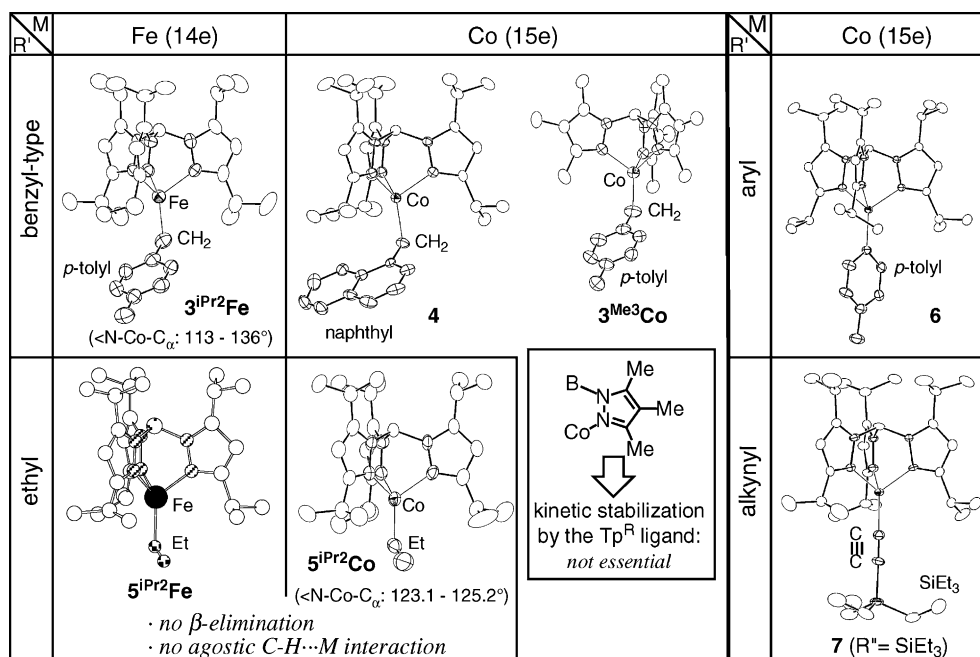
$C(=O)CH_2CH_3$ (see below) and (2) ethylene was detected from the gas phase, the reaction should give the ethylnickel intermediate, $Tp^{iPr_2}Ni-CH_2CH_3$ $5^{iPr_2}Ni$, which should undergo β -hydride elimination at ambient temperature. The η^1 -arylcobalt complex **6** was also prepared by the Grignard method, whereas the η^1 -alkynylcobalt complex **7** was obtained by the dehydrative condensation between the hydroxo complex and 1-alkyne in hexane [10]. Although the Grignard method was effective for the preparation of the alkyl and aryl complexes, we found a problem for preparation of the starting complexes [11]. When the Tp^R ligand contained bulky substituents such as isopropyl group at the 3-positions (e.g., Tp^{iPr_2}), a 1:1 reaction of MX_2 and a Tp^R anion gave the desired tetrahedral precursor, $(\kappa^3-Tp^R)M-X$, selectively, whereas reaction of the Tp^R ligand with less bulky substituents such as methyl groups (e.g., Tp^{Me_3}) usually led to the octahedral ferrocene-type 1:2 adduct $(\kappa^3-Tp^R)_2M$, which was inert toward ligand substitution. In some cases precursors with a κ^2 -leaving group (e.g., κ^2-NO_2 and κ^2-OAc), $(\kappa^3-Tp^R)M(\kappa^2-X)$, reactive enough to be alkylated by Grignard reagents were available. The κ^2 -leaving group should prevent the undesired 1:2 coupling.

The tetrahedral structures of the hydrocarbyl complexes are characterized by crystallographic as well as spectroscopic methods. The ν_{BH} vibrations appearing above 2500 cm^{-1} clearly indicate κ^3 -coordination of the Tp^R ligand [12] and the cobalt complexes showed d–d transitions in the range $500\text{--}600\text{ cm}^{-1}$ characteristic of tetrahedral cobalt(II) species. All obtained hydrocarbyl-iron and -cobalt complexes are paramagnetic, high-

spin species as determined by means of magnetic susceptibility and such an electronic configuration with 4 (Fe) and 3 (Co) unpaired electrons should be caused by the small splitting of the frontier orbitals of a tetrahedral species [13].

Molecular structures of the hydrocarbyl complexes are determined by X-ray crystallography. At first glance all obtained hydrocarbyl complexes shown in Scheme 4 are tetrahedral species with the κ^3 - Tp^R and η^1 -hydrocarbyl ligands. To be noted is that: (1) careful examination reveals no significant additional interaction between the hydrocarbyl group and the metal center (e.g., agostic interaction), leading to the structural description as tetrahedral species [14] and (2) the formation of $3^{Me_3}Co$ with the less bulky Tp^{Me_3} ligand indicates that steric shielding by bulky substituents is not essential for the present highly coordinatively unsaturated organometallic system. As for the alkynyl complexes **7**, slight distortion of the $C\equiv C-COOME$ derivative from a C_{3v} -structure to a C_s -structure (bending of the $B\cdots M-C$ linkage) suggests occurrence of $d\pi-p\pi$ interaction between the filled metal d orbital and the acetylide π^* orbital, while the $C\equiv C-SiEt_3$ derivative is essentially C_{3v} -symmetrical [10].

Reports on synthesis of related tetrahedral, coordinatively unsaturated hydrocarbyl complexes with tripodal ligands followed our communication [15] and they showed structural features and reactivity similar to those of the present $Tp^R M-R'$ complexes, while $M-C$ homolysis to lead to $M(I)$ species was noted for some of them.



Scheme 4.

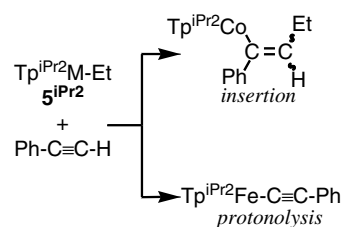
As typical examples, the reactivity of the ethyl complexes $5^{iPr_2}Fe, Co$ is summarized in Scheme 5. First of all they did not undergo β -hydride elimination, a viable decomposition process for coordinatively unsaturated hydrocarbyl species [1], even when their toluene solutions were heated to 110 °C; small amounts of ethane resulting from hydrolysis by adventitious moisture were detected but only trace amounts of ethylene resulting from β -hydride elimination were detected. 1H NMR monitoring of the thermolysis revealed that the structure of the iron complex $5^{iPr_2}Fe$ was retained even after being heated at 110 °C, whereas the cobalt complex $5^{iPr_2}Co$ was completely converted into an uncharacterized species without elimination of ethylene. The ethyl complexes 5^{iPr_2} were extremely sensitive to the moisture and air. Treatment with HCl and O_2 gave ethane and a mixture of ethanol, acetaldehyde and acetic acid, respectively; ethane should arise from protonolysis of the metal–carbon bond and the oxygenated products might be ascribed to an alkylperoxo intermediate resulting from O_2 insertion into the metal–carbon bond [3]. The alkane product was also readily obtained by hydrogenolysis at 2 atm. Carbonylation gave the propanoyl complexes **8** and the unstable ethylnickel species ($5^{iPr_2}Ni$) could be trapped by in situ carbonylation of the reaction mixture obtained from the chloro complex $1^{iPr_2}Ni$ and $EtMgBr$ as described above.

Coordinatively unsaturated hydrocarbyl species are regarded as active species of catalytic polymerization of unsaturated hydrocarbons. Before examination of the catalytic reaction the ethyl complexes 5^{iPr_2} were subjected to stoichiometric reactions with unsaturated organic compounds including alkynes, olefins, ketones and nit-

riles but only phenylacetylene reacted with them and the other substrates left 5^{iPr_2} unaffected. Reaction of the cobalt complex $5^{iPr_2}Co$ resulted in insertion of the carbon–carbon triple bond into the metal–carbon bond to give the alkenyl complex, $Tp^{iPr_2}Co-C(Ph)=C(H)-Et$, as confirmed by subsequent hydrolysis liberating 1-phenyl-1-butene, whereas the iron complex $5^{iPr_2}Fe$ was converted into the alkynyl complex, $Tp^{iPr_2}Fe-C\equiv C-Ph$, through protonation of the metal–carbon bond by the acidic $\equiv C-H$ proton, as confirmed by carbonylation leading to the diamagnetic acetylide complex, $(Tp^{iPr_2})(OC)_2Fe-C\equiv C-Ph$. Catalytic activity for ethylene polymerization was further examined, because it was reported that the related tridentate N-coordinating PBI [bis(pyridine)imine] ligands [16] were very effective for the catalysis. The chloro complexes 1^{iPr_2} and the ethylcobalt complex $5^{iPr_2}Co$ showed some catalytic activity in the presence of an excess amount of MAO [19] but their activity ($\sim 10^4$ gPE/molM; $CH_2=CH_2$: 30 kg/cm², 70 °C, 1 h) was much smaller than a typical PBI system ($>10^7$ gPE/molM). It was also found that the molecular weight distribution of the obtained polymers was bimodal suggesting formation of plural active species. The different catalytic performance could be ascribed to the different coordination properties of the N_3 -ligands (Tp^R : facial, mononegative vs. PBI: meridional, neutral).

In order to consider the origin of the stability of the coordinatively unsaturated species EHMO calculations have been carried out for a model complex, $Tp^{H_2}Fe-CH_3$ [17]. As a result, it is revealed that (1) the $Tp^{H_2}M$ fragment contains only one σ -type orbital, which can interact with the lone pair electrons of the alkyl group and (2) the five frontier orbitals (FMOs) are the d-based

$Tp^{iPr_2}M-Et$ 5^{iPr_2}	product(s)	
	yields (%)	
M	Fe	Co
Δ 110 °C, 5 hr (in toluene)	$CH_2=CH_2$	
	trace (no β -elimination)	
	CH_3-CH_3	
	10	8
HCl aq.	66	96
H_2 (2 atm, r.t.)	60	91
O_2	CH_3CH_2OH / CH_3CHO CH_3COOH	
	24 / 8 / 11	17 / 29 / 12
CO	$Tp^{iPr_2}M-C(=O)Et$ $(CO)_n$	
	62 (n=2)	64 (n=1)



but no reaction with Ph-C≡C-Ph,
 $CH_2=CH_2$, 1-hexene, ketones,
and nitriles.

ethylene polymerization
 $Tp^{iPr_2}Co-Et$ ($5^{iPr_2}Co$)
 or
 $Tp^{iPr_2}M-Cl$ (1^{iPr_2}) + MAO

effective but not so active as PBI catalysts

Scheme 5.

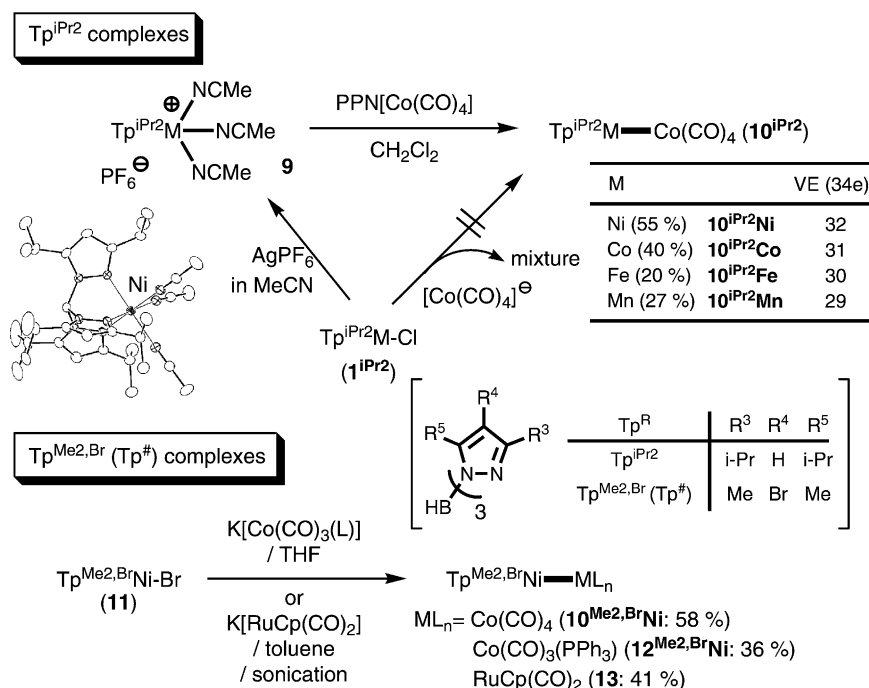
orbitals of the $\text{Tp}^{\text{H}2}\text{M}$ fragment and one of them is slightly raised in energy owing to the σ -interaction with the alkyl ligand when compared with the other orbitals. The small energy separation of the FMOs should lead to the high spin configuration with 4 (Fe) and 3 (Co) unpaired electrons as supported by the magnetic susceptibility measurements (see above). Such electronic configuration with all frontier orbitals being occupied by either electron pairs or unpaired electrons leaves no vacant orbital in the FMOs and this could be the origin of the thermal stability of the coordinatively unsaturated hydrocarbyl species. Strictly speaking, the present hydrocarbyl species are not “coordinatively unsaturated species” but “electronically unsaturated species”, the VEs of which are short of 18. Because, however, the hydrocarbyl complexes react with H_2 , O_2 and CO as mentioned above, their electronic structure should be flexible and is expected to be changed upon interaction with a substrate. In contrast to most of the previous examples of late transition metal, coordinatively unsaturated hydrocarbyl species, which are “kinetically” stabilized by bulky hydrocarbyl ligands, as mentioned in Introduction [2], the present system does not require such stabilization indicating that it is a “thermodynamically” stabilized system realized by control of the electronic structure by the Tp^{R} ligand, a tetrahedral enforcer.

3. Xenophilic complexes [18]

The successful formation of the hydrocarbyl complexes prompted us to examine metalation of the halo

precursor (Scheme 1). Initial attempts, however, were miserable. For example, treatment of $\text{Tp}^{\text{Ph,Me}}\text{M}-\text{Cl}$ ($\text{M} = \text{Co}, \text{Ni}$) with $\text{Na}[\text{Co}(\text{CO})_4]$ gave complicated mixtures, from which the cationic aquo-cobalt complex, $[\text{Tp}^{\text{Ph,Me}}\text{Co}(\text{THF})(\text{OH}_2) \cdot (\text{THF})_2][\text{Co}(\text{CO})_4]$, and the cationic tetranuclear carbonatonicel cluster compound, $[(\text{Tp}^{\text{Ph,Me}}\text{Ni})_4(\mu_4\text{-CO}_3)\text{Na}_5][\text{Co}(\text{CO})_4]$, were isolated and characterized by X-ray crystallography [18c]. To our surprise, the obtained products contained the cobaltate, $[\text{Co}(\text{CO})_4]^-$, as the counteranion of the cationic $\text{Tp}^{\text{Ph,Me}}\text{M}$ species without metal–metal bond formation. The reactions were very slow and during the very slow reaction adventitious moisture and CO_2 should interact with the $\text{Tp}^{\text{Ph,Me}}\text{M}$ fragment to give the undesired products.

The $\text{Tp}^{\text{R}}\text{M}$ fragment was then activated toward nucleophiles via conversion to cationic species (Scheme 6). Treatment of the chloro complexes $\mathbf{1}^{\text{iPr}2}$ with a silver salt in acetonitrile afforded the octahedral, cationic tris(acetonitrile) complexes $\mathbf{9}$ [20]. The cationic species $\mathbf{9}$ were reactive enough to be coupled with not only a variety of donors but also the cobaltate to give the desired metal–metal bonded dinuclear species $\mathbf{10}^{\text{iPr}2}$ with 29–32 VEs (Scheme 6). The low reactivity of $\text{Tp}^{\text{iPr}2}\text{M}-\text{Cl}$ $\mathbf{1}^{\text{iPr}2}$ should be ascribed to the bulky isopropyl substituents, because $\text{Tp}^{\text{Me}2,\text{Br}}\text{Ni}-\text{Br}$ $\mathbf{11}$ bearing the less bulky $\text{Tp}^{\text{Me}2,\text{Br}}$ ($\text{Tp}^{\#}$) ligand was directly converted to the corresponding dinuclear species $\mathbf{10}^{\text{Me}2,\text{Br}}\text{Ni}$ [21]. It was also found that the bromo precursor $\mathbf{11}$ reacted with more bulky metalates such as $\text{K}[\text{Co}(\text{CO})_3(\text{PPh}_3)]$ and $\text{K}[\text{RuCp}(\text{CO})_2]$ to give the dinuclear complexes $\mathbf{12}^{\text{Me}2,\text{Br}}$ and $\mathbf{13}$, respectively.



Scheme 6.

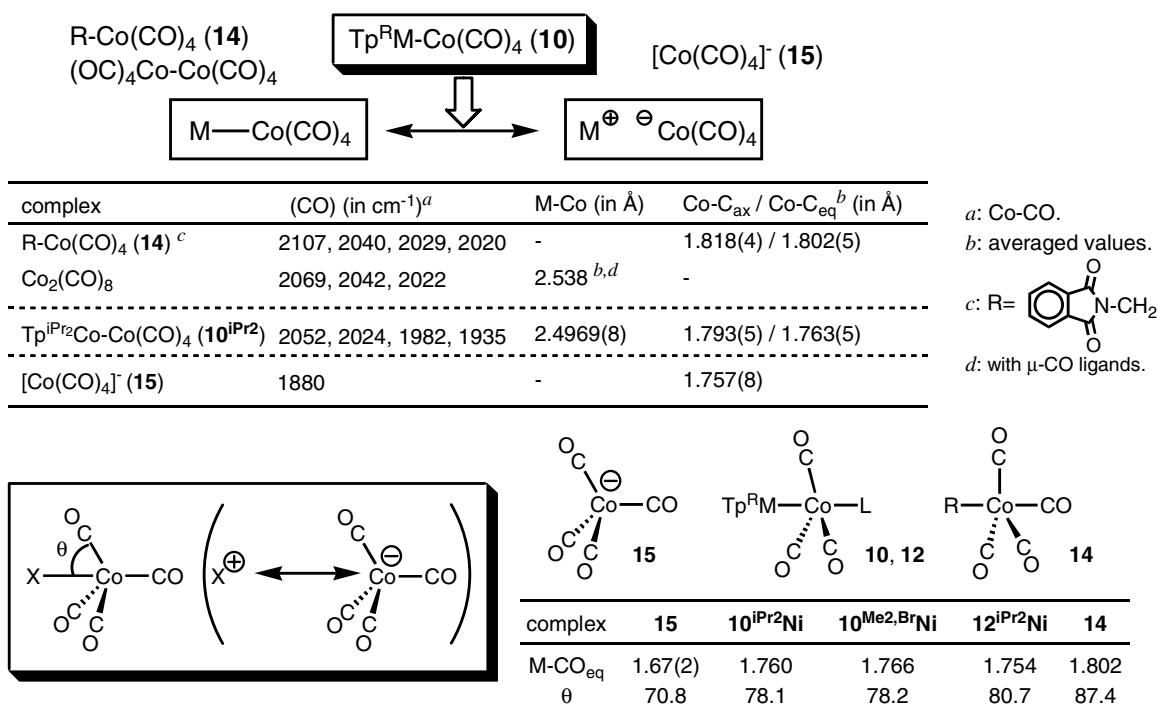
M'L _n	Co(CO) ₃ (PPh ₃)	Co(CO) ₄		RuCp(CO) ₂
Tp ^R	Tp ^{iPr2}		Tp [#]	
	<ul style="list-style-type: none"> · Tp^R: tetrahedral · Co(CO)₃(L): trigonal bipyramidal · Tp^RM-Co(CO_{eq})₃: staggered 		Kinetic stabilization is not essential.	
M-M' ^a	2.4138(9)	2.4640(8)	2.4190(9)	2.512(1)
M...CO ^{a,b}	2.622(9)	2.661(4)	2.594(6)	2.761(8)
<B...M-M' ^a	177.5(1)	179.2(1)	177.0(1)	172.4(1)

^a bond lengths in Å and bond angles in deg. ^b the shortest M...CO separation.

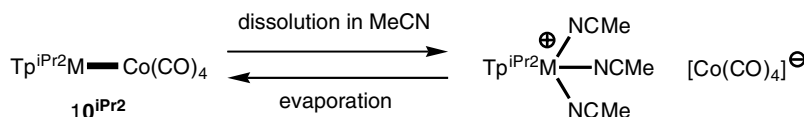
Scheme 7.

All dinuclear complexes **10**, **13** and the related PPh₃-substituted products of **10^{iPr2}** (**12^{iPr2}**; see below) were paramagnetic and characterized by means of X-ray crystallography and spectroscopic methods. As typical examples, molecular structures of three Tp^RNi-Co(CO)₃(L) derivatives **10^{iPr2}Ni**, **10^{Me2,Br}Ni** and **12^{iPr2}Ni** and Tp[#]Ni-RuCp(CO)₂ **13** are shown in Scheme 7. The core parts of the three Co complexes are isostructural.

The Tp^RCo and Co(CO)₃(L) moieties adopt tetrahedral and trigonal-bipyramidal geometry, respectively, and the three pyrazolyl rings of the Tp^R ligand and the three equatorial CO ligands of the Co(CO)₃(L) moiety are staggered to lead to a virtually C_{3v}-symmetrical structure, which is also supported by the essentially linear B...M-M' linkage. The linear Co-C-O(equatorial) linkages and the Ni...CO separation, which exceeds



Scheme 8.



Scheme 9.

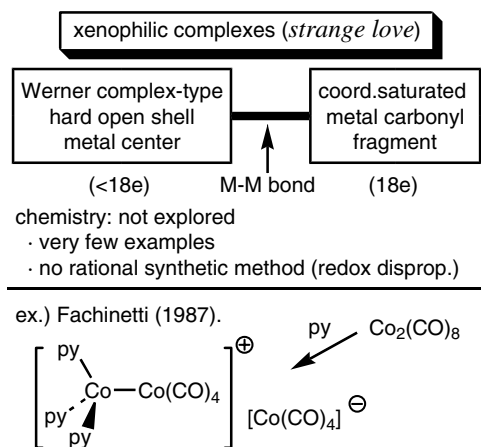
the range of bonding interaction between Ni and C, reveal no bonding interaction between the $\text{Tp}^{\text{R}}\text{Ni}$ center and the equatorial CO ligand on Co, indicating that the $\text{Tp}^{\text{R}}\text{M}$ and $\text{Co}(\text{CO})_3(\text{L})$ parts are connected only through the Ni–Co bond. The Ni–Co bond length are comparable to the sum of the covalent radii of Ni and Co. Similar structural features are noted for the other $\text{Tp}^{\text{R}}\text{M}-\text{Co}(\text{CO})_3(\text{L})$ derivatives and the Ni–Ru complex **13**. The successful formation of the $\text{Tp}^{\#}$ derivatives also reveals that kinetic stabilization by a bulky ligand such as Tp^{iPr2} is not essential for the dinuclear complexes as also pointed out for the hydrocarbonyl complexes.

A couple of representative features of $\text{Tp}^{\text{iPr2}}\text{Co}-\text{Co}(\text{CO})_4$ **10**^{iPr2}Co are compared with those of two references (Scheme 8); one with a covalent X–Co(CO)₄ linkage (the phthaloylmethyl complex **14** and $\text{Co}_2(\text{CO})_8$ [22]) and the other without such a covalent interaction ($[\text{Co}(\text{CO})_4]^-$ **15** [23]). As can be seen from the table, the $\nu(\text{CO})$ vibrations and the Co–CO distances of the dinuclear complex **10**^{iPr2}Co fall between those for the covalent and ionic species, suggesting that the M–Co bond in **10** are polarized to a considerable extent. Another measure of the contribution of the ionic form for the X–Co(CO)₄ species is the structural deviation from trigonal-bipyramidal to tetrahedral structures. As the covalent interaction between X and Co is increased, the geometry of the Co center should be changed from a tetrahedral structure to a trigonal-bipyramidal structure, and the deviation can be estimated by the angle θ ($\theta = 70.5^\circ$ for an ideal tetrahedral species; 90° for an ideal trigonal-bipyramidal species). The θ values for the dinuclear species are in the middle of the values for the two references, supporting the above-mentioned conclusion. Furthermore in accord with the structural change, as the contribution of the ionic form is diminished, the Co–CO distance is elongated, because back donation from the less negatively charged Co center to CO ligands becomes less effective.

It is remarkable that IR spectra of the cobalt complexes, $\text{Tp}^{\text{R}}\text{M}-\text{Co}(\text{CO})_3(\text{L})$, are dependent on the solvent. For example, IR spectra of $\text{Tp}^{\text{R}}\text{M}-\text{Co}(\text{CO})_4$ **10** observed in CH_2Cl_2 contain two strong $\nu(\text{CO})$ vibrations in accord with the local C_{3v} -symmetrical structure of the $\text{Co}(\text{CO})_4$ part and are very similar to those observed as KBr pellets, whereas those observed in MeCN contain a single $\nu(\text{CO})$ absorption at 1890 cm^{-1} , which is identical with the $\nu(\text{CO})$ vibration of $[\text{Co}(\text{CO})_4]^-$. The spectral change reveals M–M bond cleavage (heterolysis) upon dissolution in MeCN (Scheme 9), in other words, the

M–M bond formation (Scheme 6) is reversed to give the ion-pair, $[\text{Tp}^{\text{R}}\text{M}(\text{NCMe})_3]^+[\text{Co}(\text{CO})_4]^-$. Evaporation of MeCN regenerates the M–M bond, although partial decomposition is evident. The reversible M–M bond cleavage-recombination process can be also followed by the change of the UV–vis spectrum ($\text{Tp}^{\text{R}}\text{M}$: tetrahedral \leftrightarrow octahedral) [13]. The M–M bond heterolysis [24] induced by a coordinating solvent is another evidence for the polar nature of the M–M bond in **10**. The PPh_3 derivatives **12** also undergo the partial M–M cleavage in $\text{MeCN}-\text{CH}_2\text{Cl}_2$ (CH_2Cl_2 is added to dissolve **12**). But the Ni–Ru complex **13** decomposes upon attempted dissolution in MeCN. The extent of the M–M bond cleavage (heterolysis) is apparently correlated with the stability of the metalate to be liberated ($\text{p}K_{\text{b}}: [\text{Co}(\text{CO})_4]^- > [\text{Co}(\text{CO})_3(\text{PPh}_3)]^-$).

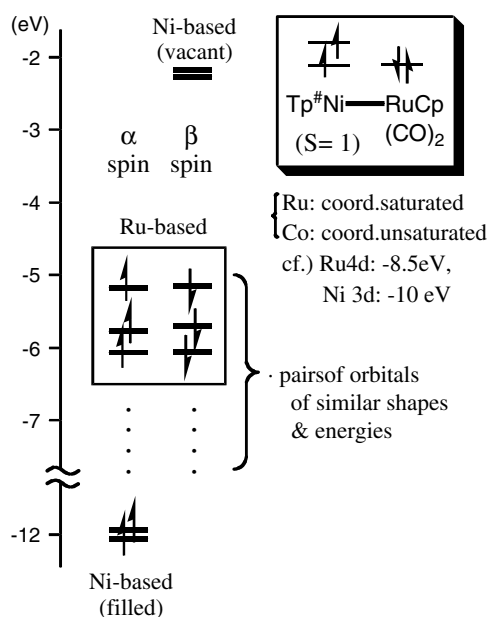
Polar metal–metal bond has attracted increasing attention, because it is expected to display unique reactivity toward polar substrates such as CO. While early-late heterobimetallics (ELHB) such as $\text{Cp}_2(\text{X})\text{Zr}-\text{RuCp}(\text{CO})_2$ and $(\text{Bu}'\text{O})_3\text{Ti}-\text{RuCp}(\text{CO})_2$ [25] can be raised as a typical example, another class of compounds called “xenophilic complexes” [26] is known (Scheme 10). Xenophilic complexes are defined as polynuclear compounds, in which a Werner complex type hard open shell metal center and a coordinatively saturated metal carbonyl fragment are connected only by a metal–metal bond. Because the two metal fragments with the different properties are connected, they are called “xenophilic (strange love)” and the M–M bond in them should be polar. The dinuclear complexes $\text{Tp}^{\text{R}}\text{M}-\text{M}'\text{L}_n$ obtained by the present study fall in this category. Chemistry of xenophilic complexes, however, has remained to be explored



Scheme 10.

mainly because of lack of a rational synthetic method. All the previous examples of xenophilic complexes including the first example reported by Fachinetti, $[(\text{py})_3\text{Co}-\text{Co}(\text{CO})_4]^+[\text{Co}(\text{CO})_4]^-$ (The cationic part is isoelectronic with **10**.) [26b], were obtained by the unpredictable redox disproportionation. Therefore the present method provides the first rational synthetic method for the unique dinuclear complexes, and the Ni–Ru complex **13** is the first example of a xenophilic complex, which involves a second row metal fragment [27].

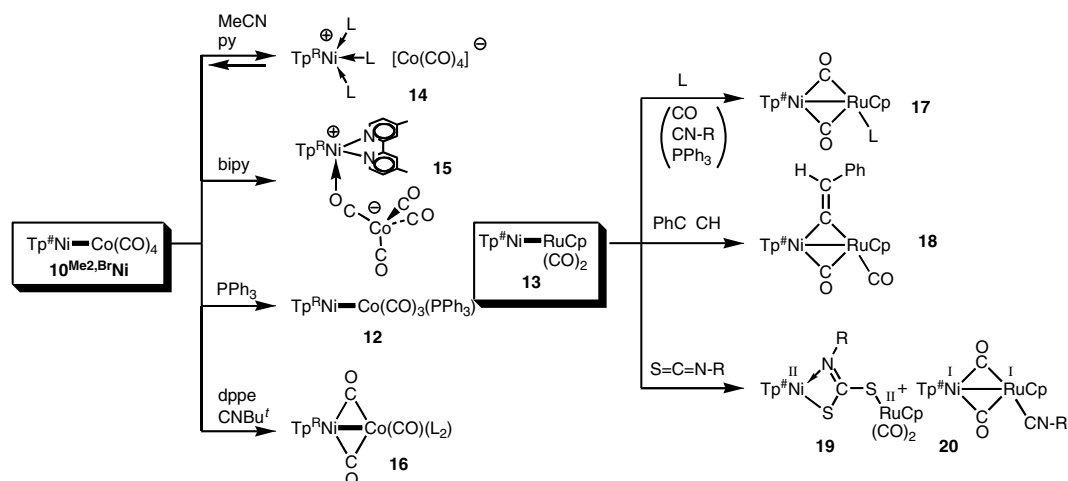
All xenophilic complexes obtained by the present study are paramagnetic, high-spin species. On the basis of (1) virtually identical CO vibrations observed for a series of the $\text{Tp}^{\text{R}}\text{M}-\text{Co}(\text{CO})_4$ -type complexes **10** irrespective of M, (2) the $\nu(\text{CO})$ values comparable to those of $\text{X}-\text{Co}(\text{CO})_3(\text{L})$ -type complexes, (3) the UV–Vis spectra very similar to those of $\text{Tp}^{\text{R}}\text{M}-\text{Cl}$ and (4) magnetic susceptibility, it is concluded that the unpaired electrons are localized on the $\text{Tp}^{\text{R}}\text{M}$ part in the dinuclear complexes in accord with the definition of xenophilic complex: $\text{Tp}^{\text{R}}\text{M}$: open shell metal center; $\text{M}'\text{L}_n$: coordinatively saturated. As a typical example, a preliminary DFT calculation has been carried out for a model complex of the Ni–Ru complex **13** [$\text{Tp}^{\text{H}2}\text{Ni}-\text{RuCp}(\text{CO})_2$] [18c]. In particular, for this complex, when the relationship of the energy levels of the first and second row metals is taken into account [Ru(4d): -8.5 eV; Ni(3d): -10 eV], it may be strange that the Ni orbitals much lower in energy than those of the filled Ru orbitals remain half-occupied. Scheme 11 shows energy levels of the molecular orbitals for the model complex obtained by the unrestricted DFT calculation [18c,27]. The six



Scheme 11.

orbitals around -5 eV are Ru-based orbitals, and shapes and energies of the α - and β -spin orbitals are very similar with each other leading to the coordinatively saturated, closed shell electronic configuration for the d^6 metal part [Ru(II)]. Contrastingly, the four Ni-based orbitals around -2 and -10 eV are different not only in their shapes but also in their energy levels, whereas the features of the other Ni-based orbital pairs (-7 to -12 eV) are similar to those of the Ru-based orbitals (similar in energy and shape). Accommodation of 208 electrons in these orbitals leads to the triplet configuration with two half-occupied Ni orbitals (-12 eV) in accord with the result of magnetic susceptibility. The big separation observed for the Ni-based α - and β -spin orbitals can be interpreted in terms of coulombic repulsion of d-electrons; it is known that coulombic repulsion for 3d-electrons is much larger than that for 4d-electrons. This unique electronic structure could originate from the coordination property of the Tp^{R} ligand, and the stability of the coordinatively unsaturated species [the number of valence electrons: for $\text{Tp}^{\text{R}}\text{M}-\text{Co}(\text{CO})_3(\text{L})$: M = Ni (32), Co (31), Fe (30), Mn (29); $\text{Tp}^{\#}\text{Ni}-\text{RuCp}(\text{CO})_2$: 32; cf. a coordinatively saturated dinuclear species: 34] can also be attributed to the lack of a vacant FMO owing to the high spin electronic configuration as discussed for the hydrocarbyl species.

The electronic structure of the dinuclear complexes is apparently similar to that of the hydrocarbyl complexes discussed above [27]. But the dinuclear complexes are found to readily react with a variety of substrates and selective reactions dependent on the properties of the substrates are observed. Scheme 12 summarizes the reactivity of the $\text{Tp}^{\#}\text{Ni}-\text{ML}_n$ -type complexes [ML_n : $\text{Co}(\text{CO})_4$ (**10**^{Me2,BrNi}), $\text{RuCp}(\text{CO})_2$ (**13**)] [18c]. First of all MeCN cleaved the M–Co bond in **10** in a heterolytic manner as mentioned above. Similar M–M heterolysis occurred by the action of N-donors such as pyridine and bipyridine in CH_2Cl_2 . The zwitterionic 4,4'-Me₂-bipy derivative **15** contained the $\mu(\kappa^1:\text{C}\kappa^1:\text{O})$ -CO (isocarbonyl) bridge but in a solution it appeared to be separated into the ion pair. These products should arise from nucleophilic addition of the hard N-donors at the hard open shell $\text{Tp}^{\#}\text{Ni}$ center. In contrast to the reaction with hard donors, soft donors initially caused CO-replacement at the $\text{Co}(\text{CO})_4$ center to give the substituted derivatives. PPh_3 gave **12** through CO-replacement, whereas dppe gave the coordinatively saturated, diamagnetic product **16** ($\text{L}_2=\text{dppe}$) through a combination of the CO-replacement and coordination of the other P part, which induced bridging of two CO ligands. The reaction with *t*-Bu–NC did not stop at the stage of the replacement but subsequent coordination of a second equivalent of the substrate led to the diamagnetic product **16** ($\text{L}=\text{CN}-\text{Bu}'$). Thus clear dependence of regiochemistry on the property of the donors is noted: hard N-donors attack the hard $\text{Tp}^{\text{R}}\text{M}$ center to lead to the M–M



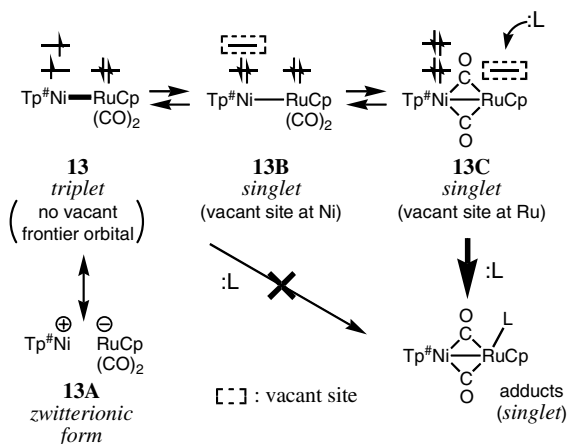
	hard donor (py, bipy, MeCN)	soft donor (PR ₃ , R-NC R-C≡C-R)
$\text{Tp}^{\text{R}}\text{Ni}=\text{Co}(\text{CO})_4$ 10 _{Me²,BrNi}	$\left[\begin{array}{c} \text{L} \\ \\ \text{Tp}^{\text{R}}\text{Ni}-\text{L} \\ \\ \text{L} \end{array} \right]^{\oplus} \left[\text{Co}(\text{CO})_4 \right]^{\ominus}$ addition to $\text{Tp}^{\text{R}}\text{M}$ leading to M-Co heterolysis	1) CO substitution 2) addition $\text{Tp}^{\text{R}}\text{Ni}-\text{Co}-\text{L} \rightleftharpoons \text{Tp}^{\text{R}}\text{Ni}-\text{Co}(\text{CO})_2$ 32e 34e
$\text{Tp}^{\text{R}}\text{Ni}=\text{RuCp}(\text{CO})_2$ 13	Ni-Ru homolysis? 1. increased covalent character 2. stability: $\text{Co}(\text{CO})_4 > \text{RuCp}(\text{CO})_2$	addition leading to 34e species $\text{Tp}^{\text{R}}\text{Ni}-\text{RuCp}(\text{CO})_2$ 34e insertion (R-N=C=S) $\text{Tp}^{\text{R}}\text{Ni}-\text{RuCp}(\text{CO})_2$

Scheme 12.

bond heterolysis, whereas soft donors initially replace a CO ligand in the $\text{Co}(\text{CO})_4$ moiety and further interaction with a donor molecule leads to the dinuclear adducts **16** with two μ -CO ligands. Similar selectivity was also observed for the reaction of the Ni–Ru complex **13** with soft donors, whereas reactions with pyridine derivatives afforded a complicated mixture of products, which apparently resulted from Ni–Ru bond homolysis. The reactions with soft donors (CO, R-NC and PPh_3) did not result in CO-replacement but addition to the Ru-center to give the diamagnetic adducts **17** analogous to **16** and the reaction with $\text{Ph}-\text{C}\equiv\text{C}-\text{H}$ gave the vinylidene complex **18** via coordination followed by 1,2-H migration. The Ni–Ru bond in **13** also interacted with heterocumulenes including isothiocyanate, which produced an equimolar mixture of the iminodithiocarbonyl complex **19** and the isonitrile complex **20**. These products should arise from a combination of disproportionation and C–S cleavage of the isothiocyanate,

although detailed reaction mechanism remained to be clarified.

It should be noted that the paramagnetic complexes **10** and **13** are converted into the diamagnetic species through interaction with diamagnetic molecules. The different spin states of the reactants (triplet for the nickel complexes) and the products (singlet) suggests that the conversions should involve a spin crossover process [28] and we propose a plausible mechanism as shown in Scheme 13. (The Ni–Ru complex **13** is taken as an example). Spin crossover at the triplet Ni center should lead to the singlet species with a vacant coordination site at the Ni center (**13B**). Subsequent switching of the coordination mode of two CO ligands ($\eta^1 \rightarrow \mu$) transfers the vacant site to the Ru center (**13C**), to which donors are added to form diamagnetic adducts. Addition to the Ni-centered vacant site followed by intramolecular migration of the donor from Ni to Ru appears to be a possible process. Because, however, intramolecular migration of



Scheme 13.

PPh_3 from one metal to the other metal may not be always viable, the addition to the Ru center should be appropriate. The CO-replacement of **10** should also involve a 34e adduct with two μ -CO ligand as an intermediate, and subsequent CO-elimination followed by $\mu \rightarrow \eta^1$ switching of the CO ligand should provide the substituted products. The high spin, xenophilic complex (e.g., **13**) is formally described not only as a resonance hybrid with the zwitterionic structure (**13A**) but also as an equilibrated mixture with the singlet, coordinatively unsaturated form (**13B,C**) resulting from spin crossover across the metal–metal bond. Thus the high-spin xenophilic complexes with no vacant coordination site can be regarded as a masked form of the coordinatively unsaturated intermediate.

4. Conclusion

The Tp^{R} ligand system shows many unique coordination features and, for the present organometallic system, it serves as a tetrahedral enforcer. Introduction of a hydrocarbyl ligand and a metal fragment into the C_{3v} -symmetrical $\text{Tp}^{\text{R}}\text{M}$ system furnishes the tetrahedral, highly electron-deficient organometallic species. The corresponding hydrocarbyl and dinuclear complexes, $\text{Tp}^{\text{R}}\text{M-R}'$ and $\text{Tp}^{\text{R}}\text{M-M}'\text{L}_n$, are readily obtained by alkylation and metalation of the halide precursors, respectively. Although the number of the valence electrons of the resultant species is much shorter than that expected for a coordinatively saturated species (for mononuclear species: 14–15e vs. 18e; for dinuclear species: 29–32e vs. 34e), they turn out to be thermally stable. In particular, the ethyl complexes $\mathbf{5}^{\text{iPr}_2}$ are stable with respect to β -hydride elimination. The tetrahedral structures of the $\text{Tp}^{\text{R}}\text{M-R}'$ and $\text{Tp}^{\text{R}}\text{M-M}'\text{L}_n$ species cause a small ligand field splitting of the FMOs to lead to a high spin configuration, which leaves no vacant coordination site, and this should be the origin of the

thermal stability of the electron deficient species. Therefore the $\text{Tp}^{\text{R}}\text{M-R}'$ and $\text{Tp}^{\text{R}}\text{M-M}'\text{L}_n$ species are “electronically unsaturated” but not “coordinatively unsaturated”. Their electronic structures, however, are flexible. Upon interaction with donors they are incorporated into the organometallic system via switching of the spin state, and selective reactions dependent on the nature of the donor molecules are observed for the dinuclear complexes. Thus the high spin species can be regarded as masked forms of coordinatively unsaturated intermediates, which are key intermediates of organometallic transformations.

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References

- [1] A. Yamamoto, *Organotransition Metal Chemistry*, Wiley-Interscience, New York, 1986;
J.P. Collman, L.S. Hegedus, J.R. Norton, R.G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, second ed., University Science Books, Mill Valley, 1987;
R.H. Crabtree, *The Organometallic Chemistry of the Transition Metals*, third ed., Wiley-Interscience, New York, 2001;
B. Cornils, W. Herrmann, *Applied Homogeneous Catalysis with Organometallic Compounds* (2 vols.), VCH, Oxford, 1996;
E.W. Abel, F.G.A. Stone, G. Wilkinson, *Comprehensive Organometallic Chemistry II*, Pergamon, Oxford, 1995.
- [2] (a) C.G. Howard, G.S. Girolami, G. Wilkinson, M. Thornton-Pett, M.B. Hursthouse, *J. Chem. Soc., Dalton Trans.* (1983) 2631;
(b) R.J. Morris, G.S. Gilorami, *Organometallics* 8 (1989) 1478;
(c) N.H. Buttrus, C. Eaborn, P.B. Hitchcock, J.D. Smith, A.C. Sullivan, *J. Chem. Soc., Chem. Commun.* (1985) 1380;
(d) R. Wehmschulte, P.P. Power, *Organometallics* 14 (1995) 3264;
(e) M.B. Hursthouse, K.J. Izod, M. Motevalli, P. Thornton, *Polyhedron* 15 (1996) 135;
(f) J. Chatt, B.L. Shaw, *J. Chem. Soc.* (1961) 285;
(g) A.R. Hermes, G.S. Girolami, *Organometallics* 6 (1987) 763;
(h) H. Müller, W. Seidel, H. Görls, *J. Organomet. Chem.* 445 (1992) 133;
(i) A. Klose, E. Solari, C. Floriani, A. Chiesi-Villa, C. Rizzoli, N. Re, *J. Am. Chem. Soc.* 116 (1994) 9123;
(j) H. Müller, W. Seidel, H. Görls, *Angew. Chem. Int., Ed. Engl.* 34 (1995) 325;
(k) W.-P. Leung, H.K. Lee, L.-H. Weng, B.-S. Luo, Z.-Y. Zhou, T.W.C. Mak, *Organometallics* 15 (1996) 1785;
(l) M.D. Fryzuk, D.B. Leznoff, E.S.F. Ma, S.J. Rettig, V.G. Young Jr., *Organometallics* 17 (1998) 2313;
(m) K.H. Theopold, J. Silvestre, E.K. Byrne, D.S. Richeson, *Organometallics* 8 (1989) 2001;

- (n) R.S. Hay-Motherwell, G. Wilkinson, B. Hussain, M.B. Hursthouse, *Polyhedron* 9 (1990) 931;
- (o) M.D. Fryzuk, D.B. Leznoff, R.C. Thompson, S.J. Rettig, *J. Am. Chem. Soc.* 120 (1998) 10126;
- (p) D. Huang, W.E. Streib, C.J. Bollinger, K.G. Caulton, R.F. Winter, T. Scheiring, *J. Am. Chem. Soc.* 121 (1999) 8087.
- [3] Abbreviations used in this paper: Tp^{R} : hydrotris(pyrazolyl)borato ligands; Tp^{iPr_2} : 3,5-diisopropylpyrazolyl derivative; Tp^{Me_3} : 3,4,5-trimethylpyrazolyl derivative; Tp^{H_2} : the non-substituted parent ligand; $\text{Tp}^{\text{Ph,Me}}$: 3-phenyl-5-methyl derivative; $\text{Tp}^{\text{Me}_2,\text{Br}}$ ($\text{Tp}^{\#}$): 3,5-dimethyl-4-bromo derivative. Compound number, superscript, and the element denote the hydrocarbyl ligand, the Tp^{R} ligand, and the central metal, respectively. For example, the $\text{Tp}^{\text{iPr}_2}\text{Fe}-p$ -methylbenzyl complex is abbreviated as $3^{\text{iPr}_2}\text{Fe}$, where **3**, iPr_2 , and **Fe** denote the *p*-methylbenzyl ligand, the Tp^{iPr_2} ligand, and the central iron metal, respectively.
- [4] S. Trofimenko, *Scorpionates The Coordination Chemistry of Polypyrazolylborate Ligands*, Imperial College Press, London England, 1999.
- [5] M. Akita, S. Hikichi, *Bull. Chem. Soc. Jpn.* 75 (2002) 1657.
- [6] (a) M. Akita, N. Shirasawa, S. Hikichi, Y. Moro-oka, *J. Chem. Soc., Chem. Commun.* (1998) 973;
- (b) N. Shirasawa, T.T. Nguyet, S. Hikichi, Y. Moro-oka, M. Akita, *Organometallics* 20 (2001) 3582.
- [7] H. Lehmkuhl, J. Näser, G. Mehler, T. Keil, F. Danowski, R. Benn, R. Mynott, G. Schroth, B. Gabor, C. Krüger, P. Betz, *Chem. Ber.* 124 (1991) 441.
- [8] N. Shirasawa, M. Akita, S. Hikichi, Y. Moro-oka, *J. Chem. Soc., Chem. Commun.* (1999) 417.
- [9] Alkylation with lithium reagents instead of Grignard reagent frequently resulted in metal exchange to give $\text{Tp}^{\text{R}}\text{Li}$.
- [10] S. Yoshimitsu, S. Hikichi, M. Akita, *Organometallics* 21 (2002) 3762.
- [11] S. Hikichi, Y. Sasakura, M. Yoshizawa, Y. Ohzu, Y. Moro-oka, M. Akita, *Bull. Chem. Soc. Jpn.* 75 (2002) 1255;
- , See the introductory part of the following paper reported by us. M. Akita, D. Ma, S. Hikichi, Y. Moro-oka, *J. Chem. Soc., Dalton Trans.* (1999) 987.
- [12] M. Akita, K. Ohta, Y. Takahashi, S. Hikichi, Y. Moro-oka, *Organometallics* 16 (1997) 4121.
- [13] (a) D.F. Shriver, P.W. Atkins, *Inorganic Chemistry*, third ed., Oxford University Press, Oxford, 1999;
- (b) F.A. Cotton, G. Wilkinson, C.A. Murillo, M. Bochmann, *Advanced Inorganic Chemistry*, sixth ed., Wiley-Interscience, New York, 1999.
- [14] The benzyl type complexes showed small distortion from a C_3 -symmetrical structure, which might be ascribed to weak interaction between the β -carbon atom and the metal center.
- [15] (a) J.L. Kisko, T. Hascall, G. Parkin, *J. Am. Chem. Soc.* 120 (1998) 10561;
- (b) J.D. Jewson, L.M. Liable-Sands, G.P.A. Yap, A.L. Rheingold, K.H. Theopold, *Organometallics* 18 (1999) 300;
- (c) P.J. Schebler, B.S. Mandimutira, C.G. Riordan, L.M. Liable-Sands, C.D. Incarvito, A.L. Rheingold, *J. Am. Chem. Soc.* 123 (2001) 331.
- [16] (a) S.D. Ittel, L.K. Johnson, M. Brookhart, *Chem. Rev.* 100 (2000) 1169;
- (b) G.J.P. Britovsek, V. Gibson, D.F. Wass, *Angew. Chem. Int., Ed. Engl.* 38 (1999) 428.
- [17] The EHMO calculation is not appropriate for calculation of open-shell species but it was expected that a rough sketch of the electronic structures could be obtained.
- [18] (a) K. Uehara, S. Hikichi, M. Akita, *Organometallics* 20 (2001) 5002;
- (b) K. Uehara, S. Hikichi, M. Akita, *Chem. Lett.* (2002) 1198;
- (c) K. Uehara, S. Hikichi, M. Akita, submitted.
- [19] Additives, $\text{AlEt}_3/(\text{PhMe}_2\text{NH})\text{B}(\text{C}_6\text{F}_5)_4(1^{\text{iPr}_2})$ and $(\text{PhMe}_2\text{NH})\text{B}(\text{C}_6\text{F}_5)_4(5^{\text{iPr}_2}\text{Co})$, were not effective.
- [20] K. Uehara, S. Hikichi, M. Akita, *Dalton Trans.* (2002) 3529.
- [21] The precursor **11** was prepared by addition of $\text{KTp}^{\#}$ to an excess amount of NiCl_2 -hydrate but reactions of other metal derivatives gave $\text{M}(\text{Tp}^{\#})_2$. See Ref. [11].
- [22] (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, G. Palyi, *Organometallics* 16 (1997) 2740;
- (b) G.G. Sumner, H.P. Klug, L.E. Alexndaer, *Acta Crystallogr.* 17 (1964) 732;
- (c) P.C. Leung, P. Coppens, *Acta. Crystallogr., Sect. B* 29 (1983) 535.
- [23] $\text{Rh}(\text{CN}-o\text{-xylyl})_4[\text{Co}(\text{CO})_4]$: I. Ojima, N. Clos, J. Donovan, P. Ingallina, *Organometallics* 10 (1991) 3211.
- [24] (a) D.A. Roberts, W.C. Mercer, G.L. Geoffroy, C.G. Pierpont, *Inorg. Chem.* 25 (1986) 1439;
- (b) D.A. Roberts, W.C. Mercer, S.M. Zahurak, G.L. Geoffroy, C.W. DeBrosse, M.E. Cass, C.G. Pierpont, *J. Am. Chem. Soc.* 104 (1982) 910.
- [25] N. Wheatley, P. Kalck, *Chem. Rev.* 99 (1999) 3379;
- C.P. Casey, *J. Organomet. Chem.* 400 (1990) 205.
- [26] (a) L.H. Gade, *Angew. Chem. Int. Ed.* 39 (2000) 2659;
- (b) G. Fachinetti, G. Fochi, T. Funaioli, P.F. Zanazzi, *Angew. Chem. Int. Ed.* 26 (1987) 680;
- (c) G. Fachinetti, G. Fochi, T. Funaioli, P.F. Zanazzi, *J. Chem. Soc., Chem. Commun.* (1987) 89;
- (d) G. Kong, G.N. Harakas, B.R. Wittlesey, *J. Am. Chem. Soc.* 117 (1995) 3502;
- (e) G.N. Harakas, B.R. Wittlesey, *J. Am. Chem. Soc.* 118 (1996) 4210;
- (f) See also: L.H. Gade, *Angew. Chem. Int. Ed.* 35 (1996) 2089.
- [27] Recent DFT calculations suggests 0 covalent bond order between the two metal centers in the xenophilic complexes suggesting that they consist of electrostatic interaction between the positively charged $\text{Tp}^{\text{R}}\text{M}$ fragment and the negatively charged $\text{M}'\text{L}_n$ fragment [18c].
- [28] (a) R.R. Schrock, K.-Y. Shih, D.A. Dobbs, W.M. Davis, *J. Am. Chem. Soc.* 117 (1995) 6609;
- (b) J.L. Detrich, O.M. Reinaud, A.L. Rheingold, K.H. Theopold, *J. Am. Chem. Soc.* 117 (1995) 11745;
- (c) R. Poli, J.N. Harvey, *Chem. Soc. Rev.* 32 (2003) 1.