Rational Synthesis and Reversible Metal−Metal Bond Scission of Heterobimetallic Xenophilic Complexes Containing an Unsupported, Polar Metal−Metal Bond, $Tp^{iPr_2}M-Co(CO)_3L$ (M = Ni, Co, Fe, Mn; L = CO, PPh_3)

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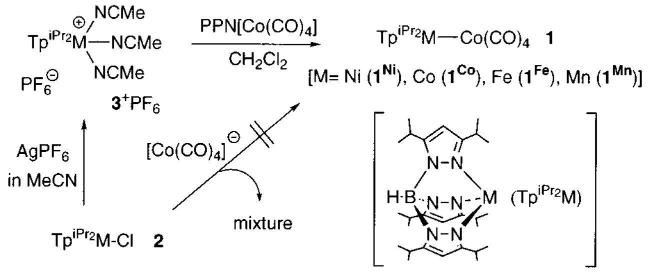
Summary: A series of heterobimetallic xenophilic complexes containing an unsupported polar metal−metal bond, $Tp^{iPr_2}M-Co(CO)_4$ (M = Ni, Co, Fe, Mn), is synthesized by treatment of the labile cationic species $[Tp^{iPr_2}M(NCMe)_3]^+$ with $PPN[Co(CO)_4]$, and the polar nature of the metal−metal bond is characterized by spectroscopic and crystallographic methods as well as by the reaction with MeCN, causing metal−metal bond heterolysis to give the ion pairs $[Tp^{iPr_2}M(NCMe)_3]^+[Co(CO)_4]^-$.

The chemistry of polar metal−metal bonds has attracted increasing attention,[1] 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[2] 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. Previous examples of xenophilic complexes resulted from a series of complicated redox disproportionation of metal carbonyls, and no rational systematic synthetic method has been developed. The hydrotris(pyrazolyl)borato ligand (Tp^R), recognized as a tetrahedral enforcer, may be used as the ancillary ligand for the “hard” part in such species.[3] In previous papers we reported the tetrahedral, highly coordinatively unsaturated alkyl complexes $Tp^{iPr_2}M-X$ (X = alkyl),[4] and the successful synthesis of such unusual organometallic species prompted us to introduce a metal fragment as the σ-ligand (X). Although a considerable number of polymetallic complexes containing a Tp^R ligand have been reported so far, very few examples of $Tp^RM-M'L_n$-type xenophilic complexes containing an unsupported M−M′ bond (M, M′ = transition metal) are known.[5−7] In most of the previous polymetallic Tp^RM complexes[6] the metal−metal bond is supported by bridging ligands (e.g. μ-CO) or the Tp^RM moiety is coordinatively saturated due to coordination of other auxiliaries (e.g. η^1-CO). Herein we wish to report the rational, systematic synthesis and characterization of a series of a new type of heterobimetallic complexes, $Tp^RM-Co(CO)_4$ (**1**; M = Ni, Co, Fe, Mn).[8]

Scheme 1



The first attempts to prepare the dimetallic complexes by treatment of the corresponding chloro complexes $Tp^{iPr_2}M-Cl$ (**2**) with cobaltates, $M'[Co(CO)_4]$ (M′ = Na, PPN), were unsuccessful (Scheme 1). The reactions were very slow and, after a prolonged reaction time, cationic aquo or carbonato complexes containing $[Co(CO)_4]^-$ as the counteranion[9] were formed as a result of interaction with adventitious moisture or carbon dioxide in the basic reaction media. To activate the $Tp^{iPr_2}M$ fragments toward nucleophiles, the chloro complexes **2** were converted to the cationic solvated complexes $[Tp^{iPr_2}M(NCMe)_3]^+$ ($\mathbf{3}^+$) via dechlorination with a silver salt in acetonitrile.[9] Complex $\mathbf{3}^+$ was so labile as to be decomposed in the absence of acetonitrile. As we expected, treatment of $\mathbf{3}^+PF_6^-$ with $PPN[Co(CO)_4]$ in CH_2Cl_2 afforded bimetallic complexes with a polar metal−metal bond, $Tp^{iPr_2}M-Co(CO)_4$ (**1**), in moderate yields.

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

[3] Trofimenko, S. *Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands*; Imperial College Press: London, 1999.

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[5] Abu Salah, O. M.; Bruce, M. I. *Aust. J. Chem.* **1977**, *30*, 2291. $CpMo(H)_2CuTp$ 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.

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

[7] A few $Tp^RM-M'L_n$-type dimetallic complexes, where M and M′ are a main-group metal and a transition metal, respectively, are known: Reger, D. L.; Mason, S. S.; Rheingold, A. L.; Haggarty, B. S.; Arnold, F. P. *Organometallics* **1994**, *13*, 5049. Reger, D. L.; Garza, D. G.; Rheingold, A. L.; Yap, G. P. A. *Organometallics* **1998**, *17*, 3624.

[8] Abbreviations used in this paper: Tp^{iPr_2}, hydrotris(3,5-diisopropylpyrazolyl)borato ligand; $Tp^{Me_2,4-Br}$, hydrotris(3,5-dimethyl-4-bromopyrazolyl)borato ligand; Tp^{Me_2}, hydrotris(3,5-dimethylpyrazolyl)borato ligand.

[9] Uehara, K.; Hikichi, S.; Akita, M. To be submitted for publication.

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Table 1. Comparison of Selected Structural Parameters for 1, $1'^{Ni}$ and 4^{Ni} [a]

	1^{Ni} [b]	1^{Co} [b]	1^{Fe}	1^{Mn}	$1'^{Ni}$	4^{Ni}
Co−M	2.4640(8)	2.4969(8)	2.504(1)	2.581(1)	2.4190(9)	2.4138(9)
Co−C1	1.785(6)	1.793(5)	1.795(7)	1.783(7)	1.790(6)	2.198(2)[c]
$Co-C_{eq}$[d]	1.760	1.764	1.777	1.767	1.766	1.75
C1−O1	1.146(7)	1.138(6)	1.124(8)	1.153(9)	1.139(8)	-
$C-O_{eq}$[e]	1.153	1.153	1.139	1.157	1.161	1.16
M−N [f]	2.002	2.030	2.057	2.150	2.011	2.006
B1···M−Co	179.2(1)	179.55(9)	177.2(1)	175.18(9)	177.0(1)	177.5(1)
M−Co−C1	176.1(2)	176.8(2)	172.4(2)	172.4(2)	173.1(2)	172.23(7)[g]
M−Co−C2	82.2(2)	81.8(2)	85.4(2)	84.2(2)	84.5(2)	85.0(2)
M−Co−C3	76.1(1)	75.9(1)	75.0(2)	74.7(2)	75.3(2)	80.9(2)
M−Co−C4	76.1(1)[h]	75.9(1)[h]	75.1(2)	74.3(2)	74.9(2)	76.3(2)

[a] Bond lengths in Å and bond angles in deg. [b] Mirror-symmetrical structure. [c] Co−P distance. [d] Averaged values of Co−(C2−C4) lengths. [e] Averaged values of CO(2−4) lengths. [f] Averaged values of M−N lengths. [g] M−Co−P1. [h] M−Co−C3*.

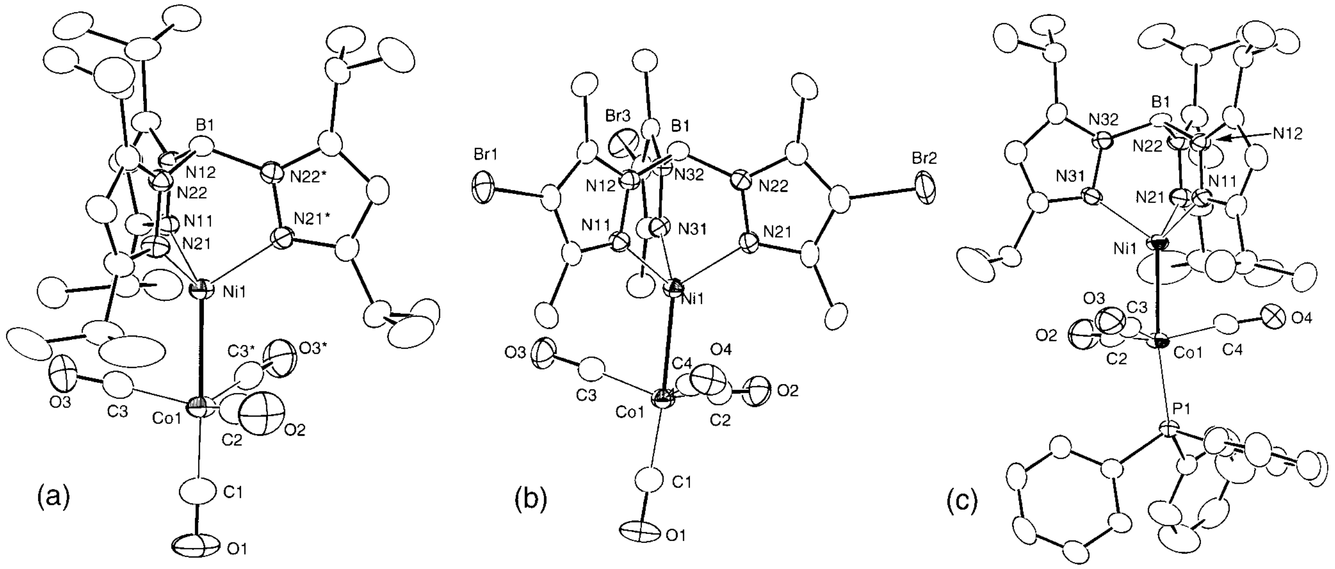
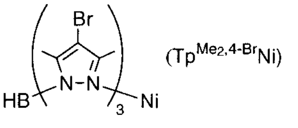


Figure 1. Molecular structures of (a) 1^{Ni}, (b) $1'^{Ni}$, and (c) 4^{Ni} drawn at the 30% probability level.

Because the polar metal−metal bond in **1** might be kinetically stabilized by the bulky Tp^{iPr_2} ligand, synthesis of a complex with a less sterically demanding methyl-substituted ligand was examined for the nickel system. Reaction of the bromide complex bearing the 3,5-dimethyl-4-bromo derivative $Tp^{Me_2,4-Br}Ni-Br$ ($\mathbf{2'^{Ni}}$)[8,9] with $K[Co(CO)_4]$ produced the corresponding bimetallic complex $\mathbf{1'^{Ni}}$ (eq 1) in contrast to the sluggishness of the Tp^{iPr_2} derivative **2** mentioned above, which could be ascribed to the bulkiness and electron-donating property of the Tp^{iPr_2} ligand. Synthesis of the analogue with the 3,5-dimethylpyrazolyl derivative (Tp^{Me_2})[8] via similar procedures, however, has not met with success, suggesting that the Lewis acidic property of the metal center in Tp^RM-X is another important factor for the metal−metal bond formation. Although complexes **1** and $\mathbf{1'^{Ni}}$ are air- and moisture-sensitive, no significant difference has been observed for their thermal stabilities and, therefore, kinetic stabilization is not essential for the polar metal−metal bond in $Tp^RM-Co(CO)_4$.

$$\underset{\mathbf{2'^{Ni}}}{Tp^{Me_2,4\text{-}Br}Ni\text{-}Br} \xrightarrow[THF]{K[Co(CO)_4]} \underset{\mathbf{1'^{Ni}}\ (58\ \%\ yield)}{Tp^{Me_2,4\text{-}Br}Ni-Co(CO)_4} \qquad (1)$$



($Tp^{Me_2,4\text{-}Br}Ni$)

IR data for **1** and $\mathbf{1'^{Ni}}$ (ν_{CO} pattern peculiar to C_{3v}-symmetrical $X-Co(CO)_4$ species and ν_{BH} indicative of κ^3-Tp^{iPr_2} coordination)[10,11] suggest formation of the desired structures, which have been characterized by X-ray crystallography.[12] The five complexes turn out to be isostructural, as compared in Table 1, and ORTEP views of $\mathbf{1^{Ni}}$ and $\mathbf{1'^{Ni}}$ (Figure 1a,b) show the virtually C_{3v}-symmetrical structure with the staggered conformation of the three pz^R rings and the three equatorial CO ligands. The M−Co vector is superimposed on the 3-fold axis of the TpNi moiety, as judged by the B1···M−Co1 angle (175.18−179.55°). 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 $Tp^{iPr_2}M$ moiety electron-deficient, as in the alkyl complexes.[4] We wish to point out that one of the three $M-Co-CO_{equatorial}$ angles (M−Co−C2) is larger than the other two angles, although the reason for the slight distortion from a C_{3v} structure is not clear at the moment. In the series of the **1**-type complexes the increase in 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. It should be noted that (1) the Co−

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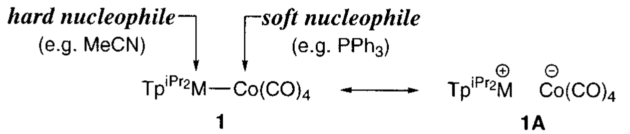
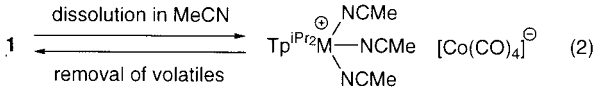
(10) Akita, M.; Ohta, K.; Takahashi, Y.; Hikichi, S.; Moro-oka, Y. *Organometallics* **1997**, *16*, 4121.

Scheme 2



Co distance in $\mathbf{1^{Co}}$ is comparable to the covalent Co−Co bond length in $Co_2(CO)_8$ with three μ-CO ligands (2.522 Å)[13] and (2) $\mathbf{1^{Co}}$ is isoelectronic with the cationic part of $[(py)_3Co{-}Co(CO)_4]^+[Co(CO)_4]^-$ reported by Fachinetti,[2a] which has been regarded as the first example of a xenophilic complex.[2b] Thus, the electron-deficient dimetallic complexes **1** with 29 ($\mathbf{1^{Mn}}$), 30 ($\mathbf{1^{Fe}}$), 31 ($\mathbf{1^{Co}}$), and 32 ($\mathbf{1^{Ni}}$, $\mathbf{1'^{Ni}}$) valence electrons turn out to be xenophilic complexes with the open-shell Tp^RM fragment.

The M−M bonds in **1** are polar, as indicated by their CO vibrations and Co−CO distances,[11] which are intermediate between those for $R{-}Co^I(CO)_4$ with a covalent Co−C bond (R = phthalimidoylmethyl; 2107, 2040, 2029, 2020 cm^{-1};[14a] 1.818 (axial), 1.802 Å (equatorial)[14b])[14a] and the ionic species $[Co^{-I}(CO)_4]^-$ (1880 cm^{-1};[14c] 1.756 Å[14b]).[14d] The polar nature of the M−M bond, which is interpreted in terms of the contribution of the ionic form **1A** (Scheme 2), is also verified by a chemical reaction. Dissolution of **1** in MeCN caused M−M bond heterolysis to form the ion pairs $[Tp^{iPr_2}M(NCMe)_3]^+[Co(CO)_4]^-$, the UV−vis and IR features of which were identical with those of the starting compounds $\mathbf{3}^+$ (UV−vis) and PPN[Co(CO)$_4$] (IR; ν_{CO}), confirming the presence of the corresponding metallic components in the solution (eq 2). Removal of the volatiles under reduced pressure regenerated **1**, although partial decomposition was evident. The bond heterolysis should be promoted by nucleophilic attack of MeCN at the positively charged $Tp^{iPr_2}M$ moiety and ionic cleavage of a metal−metal bond has several precedents.[15] In contrast, addition of PPh$_3$ to **1** resulted in selective CO displacement at the Co(CO)$_4$ moiety to give the substituted products **4** (eq 3). These results reveal the ambident character of **1**; hard and soft nucleophiles attack the hard open-shell Tp^RM moiety and the metal carbonyl fragment, respectively, in a specific manner (Scheme 2). The core part of the phosphine-substituted heterometallic complex $\mathbf{4^{Ni}}$ characterized crystallographically (Figure 1c)[12] is isostructural with that of $\mathbf{1^{Ni}}$, while the Ni−Co distance in $\mathbf{4^{Ni}}$ is shorter than that in $\mathbf{1^{Ni}}$ (Table 1) due to an increase of electron density at the Co(CO)$_3$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 $\mathbf{4^{Ni,Co}}$, however, was also cleaved in $CH_3CN{-}CH_2Cl_2$, judging from the IR data.[16] The substitution caused a blue shift of a couple of the UV−vis absorptions, which could be assigned to MMCT transitions. It is also notable that $\mathbf{4^{Ni}}$ could not be obtained by reaction of $\mathbf{3^{Ni+}}$ with the more nucleophilic but bulkier cobaltate Na[Co(CO)$_3$(PPh$_3$)], indicating that the sterically demanding Tp^{iPr_2} ligand prevented the metal−metal bond formation.



$$\mathbf{1} \underset{\text{removal of volatiles}}{\overset{\text{dissolution in MeCN}}{\rightleftarrows}} Tp^{iPr_2}\overset{\oplus}{M}(NCMe)_3 \quad [Co(CO)_4]^{\ominus} \qquad (2)$$

$$\mathbf{1} \xrightarrow[\text{toluene}]{PPh_3} Tp^{iPr_2}M{-}Co(CO)_3(PPh_3) \ \ \mathbf{4} \qquad (3)$$

[M= Ni ($\mathbf{4^{Ni}}$), Co ($\mathbf{4^{Co}}$), Fe ($\mathbf{4^{Fe}}$), Mn ($\mathbf{4^{Mn}}$)]

In conclusion, we have developed a rational synthetic method for a series of heterobimetallic xenophilic complexes with a polar M−M bond and the polar nature of the M−M bond has been characterized by (i) X-ray crystallography, (ii) comparison with the related $Tp^{iPr_2}M{-}X$ and $X{-}Co(CO)_4$ species, and (iii) the reversible M−M heterolysis induced by a hard donor. Thus, the Tp^RM fragment serves as a versatile component of xenophilic complexes. Further study on the reactivity of the obtained xenophilic species is now under way, and the result will be reported in due course.

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Supporting Information Available: Experimental procedures for X-ray crystallography and crystallographic results. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Synthesis of $\mathbf{1^{Ni}}$: to a mixture of $\mathbf{3^{Ni+}}PF_6^-$ (300 mg, 0.379 mmol) and PPN[Co(CO)$_4$] (403 mg, 0.568 mmol) was added CH$_2$Cl$_2$ (10 mL), and the resultant solution was stirred for 2 h at ambient temperature. After removal of the volatiles under reduced pressure, the residue was extracted with ether and deep purple crystals of $\mathbf{1^{Ni}}$ (143 mg, 0.206 mmol, 55% yield) were obtained by crystallization at −20 °C. Data for $\mathbf{1^{Ni}}$ are as follows. IR (KBr): ν_{BH} 2534 (m); ν_{CO} 2052 (s), 1982 (vs), 1937 (vs) cm^{-1}. IR (CH$_2$Cl$_2$): 2051 (s), 1980 (s), 1947 (vs). IR (CH$_3$CN): 1892 cm^{-1}. UV−vis (λ_{max}/nm (ϵ/M^{-1} cm^{-1}), in CH$_2$Cl$_2$): 922 (100), 867 (90), 544 (460), 488 (230). $\mu_{eff} = 2.75\ \mu_B$. Anal. Calcd for $C_{31}H_{46}BN_6O_4CoNi$: C, 53.56; H, 6.67; N, 12.09. Found: C, 53.34; H, 6.91; N, 12.19. Synthesis of $\mathbf{4^{Ni}}$: a toluene solution of $\mathbf{1^{Ni}}$ (300 mg, 0.432 mmol) and PPh$_3$ (113 mg, 0.432 mmol) was stirred for 3 h at ambient temperature. Filtration through a Celite plug followed by concentration of the filtrate and crystallization from toluene−pentane gave $\mathbf{4^{Ni}}$ as dark red crystals (95 mg, 0.102 mmol, 35% yield). Data for $\mathbf{4^{Ni}}$ are as follows. IR (KBr): ν_{BH} 2534 (w); ν_{CO} 1979 (m), 1907 (vs), 1896 (vs) cm^{-1}. IR (CH$_2$Cl$_2$): 1978 (m), 1905 (vs), 1892 (vs) cm^{-1}. IR (1/1 CH$_3$CN/CH$_2$Cl$_2$): 1927 (m), 1892 (vs), 1838 (vs) cm^{-1}. UV−vis (λ_{max}/nm (ϵ/M^{-1} cm^{-1})): 955 (130), 520 (630), 404 (720). $\mu_{eff} = 3.16\ \mu_B$. Anal. Calcd for $C_{48}H_{62}BN_6O_3PCoNi$: C, 62.33; H, 6.62; N, 9.04. Found: C, 61.88; H, 6.76; N, 8.99. Spectroscopic and analytical data for other complexes are included in Supporting Information.

(12) X-ray diffraction measurements were made on a Rigaku RAXIS IV imaging plate area detector at −60 °C. Details of the experimental procedures and the results are described in the Supporting Information.

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

(16) (a) Because complexes $\mathbf{4^{Co,Ni}}$ were sparingly soluble in CH$_3$CN, the IR measurements were done in a CH$_3$CN/CH$_2$Cl$_2$ mixed solvent system (1/1).