Tetranuclear Complexes Based on a Dynamic Metal−Metal Linkage, $[(\mu_4\text{-X})Rh_4(CO)_4(PNNP)_2]^{n+}$ (X/*n* = RC≡C/1 (Acetylide), C_2/0 (Dicarbide))

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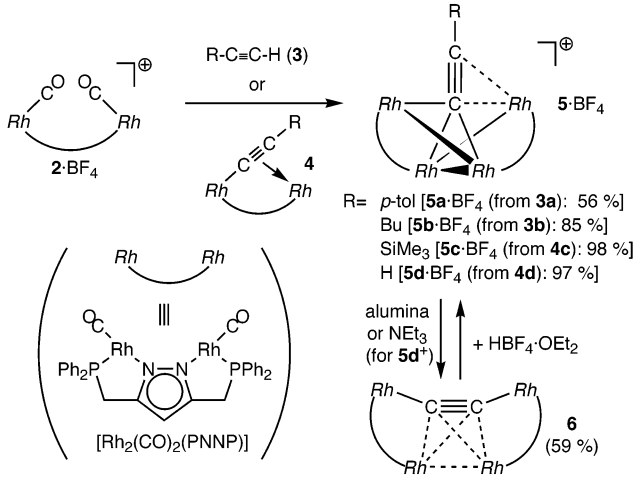
Summary: *Tetrarhodium complexes with a PNNP auxiliary,* $[(\mu_4\text{-X})Rh_4(CO)_4(PNNP)_2]^{n+}$ *(X/n = RC≡C/1 (acetylide),* C_2*/0 (dicarbide); PNNP = 3,5-bis((diphenylphosphino)methyl)pyrazolato), are integrated mainly through M−X interactions and exhibit unique dynamic behavior associated with reversible metal−metal bond cleavage and recombination processes.*

The chemistry of transition-metal cluster compounds constitutes a substantial part of organometallic chemistry, and previous studies have revealed a variety of structural motifs not only for the coordination mode of the organyl moiety but also for the metal framework.[1] Metal−metal bonds have been regarded as the major structural motif for the metal framework. However, little attention has been paid to polynuclear organometallic systems, which are not supported by metal−metal bonds, in contrast to relevant inorganic systems such as polyoxometalates. We have been studying polynuclear complexes containing a PNNP ligand (PNNP = 3,5-bis((diphenylphosphino)methyl)pyrazolato).[2] This PNNP ligand has the feature that the two metal centers bridged by it are at a distance longer than the M−M bonding interaction and, therefore, a metal−metal bond cannot be formed between them. In a previous paper[3] we reported the tetranuclear μ_4-hydride complex $[(\mu_4\text{-H})Rh_4(CO)_4(PNNP)_2]^+$ (**1**$^+$), in which the four metal centers are bound together only through H−Rh interactions. Herein we wish to report the unique tetranuclear complexes, which turn out to be dynamic with respect to cleavage and recombination of metal−metal bonds.

Reaction of the labile cationic dinuclear tetracarbonyl complex $[Rh_2(CO)_4(PNNP)]BF_4$ (**2**·BF_4) with 1-alkyne (**3**; R = *p*-tol, Bu)[4] or the dinuclear μ-acetylide complex $[(\mu\text{-}\eta^1{:}\eta^2\text{-RC≡C})Rh_2(CO)_2(PNNP)]$ (**4**; R = $SiMe_3$, H),[5] yielded the deep purple-red products **5**·BF_4 in good yields (Scheme 1).[6,7] Although the ESI-MS spectra of **5**·BF_4 revealed the formation of cationic tetranuclear acetylide

Scheme 1



complexes with the composition of $[(RC≡C)Rh_4(CO)_4(PNNP)_2]^+$ through a 1/2 RC≡C/Rh_2(PNNP) coupling, unique but complicated dynamic behavior was observed for them. For example, the *p*-tolylethynyl complex **5a**·BF_4[6] showed a single ^{31}P NMR resonance (δ_P 56.3) at 25 °C, which separated into two signals below −42 °C (Figure 1a). The two signals as well as the different P−Rh coupling constants (**5a**$^+$: 195 Hz (δ_P 64.5); 171 Hz (δ_P 61.4)) revealed that **5a**$^+$ contained two types of rhodium atoms located in different environments. No further change was observed, even when the sample was cooled to −90 °C. The fact that the J_{P-Rh} value at 25 °C (183 Hz) is precisely the average of the J_{P-Rh} values observed at −90°C ((195 + 171)/2 = 183) confirms that the single δ_P signal at 25 °C results from coalescence of the two signals observed at low temperatures. In accord with the change in the ^{31}P NMR spectrum, the acetylide α-carbon signal, which was observed at 25 °C as a quintet of quintets due to coupling with the four equivalent RhP units (Figure 1b), changed into an irresolvable multiplet at low temperatures, whereas the β-carbon signal appeared as a broad signal irrespective of temperature, presumably due to a weaker interaction with the $[Rh_2(PNNP)]_2$ moiety compared with that of the α-carbon atom. The lack of $^1J_{C-H}$ coupling for the α-carbon signal clearly indicated formation of an acetylide cluster compound resulting from deprotonation of the ≡CH moiety (from **3**).[8] Similar spectroscopic features were noted for the other complexes.[6] These spectroscopic features suggest that (1) the Rh_4 metal framework is unsymmetrical with respect to the

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(2) Schenk, T. G.; Downs, J. M.; Milne, C. R. C.; Mackenzie, P. B.; Boucher, H.; Whelan, J.; Bosnich, B. *Inorg. Chem.* **1985**, *24*, 2334. Schenk, T. G.; Milne, C. R. C.; Sawyer, J. F.; Bosnich, B. *Inorg. Chem.* **1985**, *24*, 2338. See also: Bosnich, B. *Inorg. Chem.* **1999**, *38*, 2554.

(3) Tanaka, S.; Akita, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 2865.

(4) Complexes **5a**,**b**$^+$ were also obtained from **2**$^+$ and the dinuclear acetylide complexes **4a**,**b**, respectively.

(5) Complexes **4** were prepared by treatment of **2**·BF_4 with LiC≡CR. Tanaka, S.; Inagaki, A.; Akita, M. To be submitted for publication.

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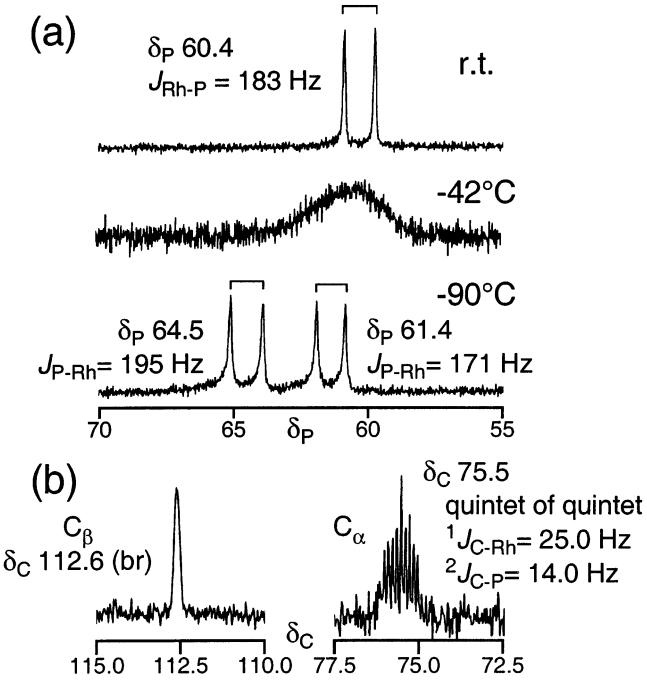


Figure 1. NMR spectra for **5a**·BF_4 observed in CD_2Cl_2: (a) variable-temperature ^{31}P NMR spectra observed at 81 MHz; (b) ^{13}C NMR spectra for the C≡C part observed at 25 °C at 100 MHz.

RC≡C moiety but exhibits dynamic behavior that averages all Rh coordination environments at higher temperatures and (2) the α- and *β*-carbon atoms of the acetylide part are *σ*- and *π*-bonded to the Rh_4 framework, respectively: i.e., μ_4-$\eta^1(C_\alpha)$ and $\eta^2(C_\alpha{\equiv}C_\beta)$ coordination.

The molecular structure of the *p*-tolylethynyl complex **5a**·BPh_4 was determined by X-ray crystallography (Figure 2a).[10] Although the four rhodium atoms are arranged in a butterfly-like array,[1] it should be noted that the two Rh···Rh distances (Rh1···Rh2 = 3.6767(4) Å; Rh3···Rh4 = 3.7592(6) Å)[9] exceed the range of the bonding interaction in contrast to the other Rh−Rh distances of ca. 2.9 Å. The metal array observed for **5a**$^+$ is best described as a folded Z-shaped linkage. As is suggested by the spectroscopic data, the α-carbon atom of the acetylide ligand forms *σ*-bonding interactions with all four Rh centers and the C≡C moiety is *π*-bonded to one of the wingtip metal atoms, leading to the μ_4-η^1-(C_α):$\eta^2(C_\alpha{\equiv}C_\beta)$ coordination.

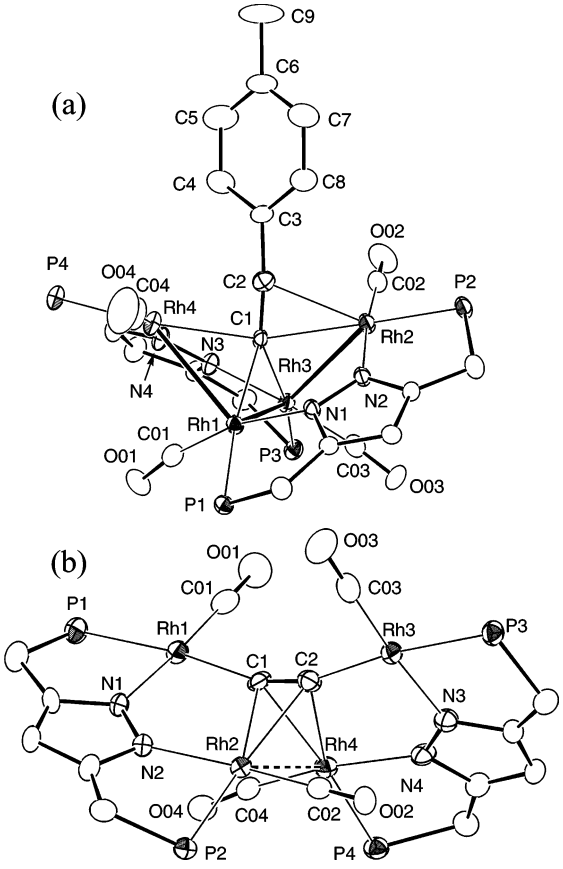


Figure 2. ORTEP views for (a) the cationic part of **5a**·BPh_4 and (b) **6**. Phenyl groups are omitted for clarity. Selected bond distances (in Å) and bond angles (in deg) are as follows. **5a**·BPh_4: Rh1−Rh3 = 2.8925(4), Rh1−Rh4 = 2.9474(5), Rh2−Rh3 = 2.9732(5), C1−C2 = 1.249(7), C1−Rh1 = 2.151(4), C1−Rh2 = 2.309(4), C1−Rh3 = 2.223(4), C1−Rh4 = 2.335(4), C2−Rh2 = 2.386(5), C2···Rh4 = 2.555(5); Rh3−Rh1−Rh4 = 80.13(2), Rh1−Rh3−Rh2 = 77.62(1), C1−C2−C3 = 172.3(5). **6**: C1−C2 = 1.22(1), C1−Rh1 = 2.04(1), C1−Rh2 = 2.438(8), C1−Rh4 = 2.396(7), C2−Rh2 = 2.408(7), C2−Rh3 = 2.06(1), C2−Rh4 = 2.441(8), Rh1···Rh2 = 3.815(1), Rh1···Rh4 = 3.762(1), Rh2···Rh3 = 3.7826(8), Rh2−Rh4 = 3.1727(9), Rh3···Rh4 = 3.849(1); Rh1−C1−C2 = 163.4(7), Rh3−C2−C1 = 164.0(7), Rh1−C1−Rh2 = 116.5(3), Rh3−C2−Rh4 = 117.2(4), C1−Rh2−C2 = 29.2(3), C1−Rh4−C2 = 29.2(3).

The temperature-dependent NMR behavior of **5**$^+$ described above has been interpreted in terms of a combination of flipping of the acetylide ligand (path a) and reorganization of the folded Z-shaped metal linkage (path b) (Scheme 2), although a spectrum at the slow exchange limit, which is consistent with **5**$^+$ with no element of symmetry, has not been obtained. The two processes can be regarded as modified versions of the well-documented windshield wiper motion of the acetylide ligand: between the wingtip metal atoms (path a) and between the intra-PNNP-unit wingtip−hinge metal atoms (path b). The subtle difference in the C2−Rh2 and C2−Rh4 distances (∼0.17 Å) in **5a**·BPh_4 suggests

(6) For experimental details, see the Supporting Information.

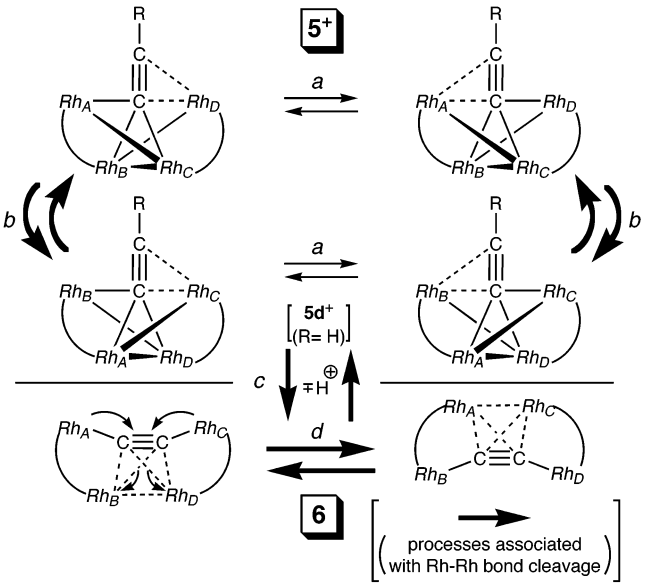
(7) We also attempted synthesis of the Ir_4 and Rh_2Ir_2 derivatives. They were detected by ESI-MS and ^{31}P NMR but could not be isolated, owing to their lability.

(8) The formation of **5**$^+$ from **2** and **3** should proceed by way of the dinuclear intermediate **4**.[4] The viability of a deprotonation process in the formation of **5** from 1-alkyne (**3**) is supported by the observation that the reaction was promoted by a basic solvent; i.e., the reaction in acetone was faster and cleaner than that in CH_2Cl_2.

(9) Except for the unusually long Rh−Rh separation observed for a dodecarhodium cluster compound (3.567 Å),[9a] Rh−Rh distances are shorter than 3.3 Å. For example, the longest Rh−Rh distance in dinuclear complexes cited in the CSD is found for $[Rh_2(CN\text{-}C_6H_4\text{-}p\text{-}F)_8]^{2+}$ (3.293 Å).[9b] (a) Albano, V. G.; Chini, P.; Martinengo, S.; Sansoni, M.; Strumolo, D. *J. Chem. Soc., Dalton Trans.* **1978**, 459. (b) Endres, H.; Gottstein, N.; Keller, H. J.; Martin, R.; Rodemer, W.; Steiger, W. *Z. Naturforsch., B* **1979**, *34*, 827.

(10) X-ray diffraction measurements were made on a Rigaku RAXIS IV imaging plate area detector with graphite-monochromated Mo Kα radiation at −60 °C. Crystal data for **5a**·BPh_4: $C_{95}H_{77}BN_4O_4P_4Rh_4$, fw 1884.94, monoclinic, space group $P2_1/a$, a = 17.9746(3) Å, b = 27.7046(6) Å, c = 16.6001(3) Å, β = 90.8460(10)°, V = 8265.6(3) Å^3, Z = 4, d_{calcd} = 1.515 g cm^{-3}, μ = 0.917 mm^{-1}, R1 (wR2) = 0.043 (0.127) for the 11 068 unique data with $I > 2\sigma(I)$ and 1010 parameters. Crystal data for **6**: $C_{64}H_{50}N_4O_4P_4Rh_4$, fw 1474.64, monoclinic, space group $P2_1/c$, a = 22.608(3) Å, b = 19.320(3) Å, c = 14.927(4) Å, β = 110.979(4)°, V = 6087(1) Å^3, Z = 4, d_{calcd} = 1.609 g cm^{-3}, μ = 1.218 mm^{-1}, R1 (wR2) = 0.068 (0.193) for the 8137 unique data with $I > 2\sigma(I)$ and 721 parameters. CCDC: 218771 (**5a**·BPh_4) and 218772 (**6**).

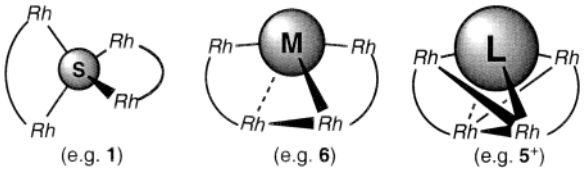
Scheme 2



that the lower energy process, which could not be frozen out even at −90 °C, should be ascribed to the least-motion process (path a). It is notable that the higher energy process (path b) involves reversible cleavage and recombination of the metal−metal bonds.

The NMR data for the ≡CH part of the ethynyl complex **5d**·BF_4 (δ_H 6.82; J_{C-H} = 237 Hz) suggests its acidic character. Accordingly, treatment of **5d**·BF_4 with alumina or NEt_3 resulted in deprotonation to give the neutral C_2 complex **6**,[11] and the resultant product **6** reverted to **5d**·BF_4 upon protonation with HBF_4·OEt_2 (Scheme 1). The simple NMR features for **6** (single δ_C(C≡C) and δ_P signals), which did not change even when the sample was cooled as low as −90 °C,[6] suggested formation of a symmetrical structure, and the ^{13}C NMR signal for the C_2 bridge was located at δ_C 98.9 (multiplet). X-ray crystallography of **6**[10] (Figure 1b) revealed the tetranuclear μ_4-dicarbide structure, in which the C_2 bridge interacts with each Rh_2(PNNP) fragment in a μ-η^1:η^2 fashion. The C≡C length is 1.22(1) Å, and the structure of the dinuclear moiety (μ-C_2)[Rh_2(PNNP)] is found to be similar to that of the dinuclear complex **4**.[5] Complex **6** is a rare example of such a type of compound ((μ_4-η^1:η^1:η^2:η^2-C_2)M_4)[13] but, in comparison with the previous examples, the (μ_4-C_2)M_4 moiety is folded to a considerable extent. The dihedral angle between the C1−C2−Rh2 plane and the C1−C2−Rh4 plane is 94.8°, which is substantially more acute than the corresponding dihedral angle in [(μ_4-C_2)Cu_4(Ph_2-Ppzpy)$_2$]$^{2+}$ (129.0°).[13b] In addition, because the Rh2−Rh4 separation (3.1727(9) Å) falls in the longer end of Rh−Rh bond lengths,[9] the folding should result from the bonding interaction between the Rh2 and Rh4 atoms.[12] The inconsistency between the virtually C_2-symmetrical solid-state structure with two different P environments and the single ^{31}P NMR signal is due to dynamic behavior via oscillation of the C_2 ligand, i.e., concurrent switching of the η^1 and η^2 coordination (d in Scheme 2),[13c] where the σ-bonded metal centers in one structure ($Rh_{A,C}$) move to the π-bonded sites in the other structure. The activation barrier for the fluxional process should be very low, because the process was not frozen out even at −90 °C. It is notable that (i) the fluxional behavior of **6** involves a Rh−Rh bond cleavage process and (ii) the deprotonation of **5d**$^+$ causes metal−metal bond cleavage to form **6**, protonation of which regenerates M−M bonds to give **5d**$^+$ (Scheme 1).

Scheme 3



In summary, we have presented the synthesis and unique properties of the dynamic tetrarhodium complexes [(μ_4-X)Rh_4(CO)$_4$(PNNP)$_2$]$^{n+}$ (**5**$^+$ and **6**; Scheme 2). The fluxional processes involve reversible cleavage and recombination of the Rh−Rh bonds (paths b and d), and the Rh_4 species **5d**$^+$ and **6** are interconverted with each other via the protonation−deprotonation cycle associated with cleavage of the Rh−Rh interaction (path c). The structure of the metal framework is dependent on the size of the bridging ligand (Scheme 3); i.e., a bulkier substrate should cause deformation of the symmetrical structure to bring metal atoms closer and form metal−metal bonds, and thus it was concluded that the polynuclear structures are integrated mainly through the M−X interactions rather than the M−M interactions. As a result, the metal−metal bonds become dynamic. Although non-M−M-bonded polynuclear structures are known for group 11 metal species,[1] examples of other group metal complexes are still rare[1] and dynamic behavior via a reversible M−M cleavage process has few precedents.[14] Further studies using related ligand systems are now in progress.

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Supporting Information Available: Text and tables giving experimental and crystallographic details; crystallographic data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

OM034315+

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(12) It is not always easy to determine the presence of a M−M bond only on the basis of the M−M distance. The maximum Rh−Rh bond length is 3.3 Å,[9] whereas the covalent radius of Rh is 1.25 Å.[12a] In the case of **6**, the Rh2−Rh4 bonding interaction (3.1727(9) Å) should cause weak Rh2···C04 and Rh4···C02 interactions, leading to the slightly bent structure of the Rh2−C02−O02 (173.4(7)°) and Rh4−C04−O04 moieties (172.4(7)°) (cf. Rh1−C01−O01 = 179(1)° and Rh3−C03−O03 = 179(1)°). The steric repulsion among the CO ligands, which project in the same direction as the μ-C_2 ligand does, may arrange the two rhodium centers close enough for bonding interaction leading to the folded structure. Emsley, J. *Elements*, 2nd ed.; Oxford University Press: Oxford, U.K., 1998.

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(14) See, for example: Akita, M.; Terada, M.; Moro-oka, Y. *Organometallics* **1992**, *11*, 1825 and references therein.