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Linearly Aligned Metal Clusters: Versatile Reactivity and Bonding Nature of Tetrametal M–Mo–Mo–M Complexes (M = Pt, Pd, Ir, and Rh) Supported by 6-Diphenylphosphino-2-pyridonato Ligand

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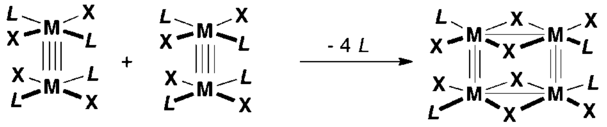
A tridentate ligand, pyphos (6-diphenylphosphino-2-pyridonato), was utilized to prepare tetrametal complexes since this ligand has unique coordinating sites comprised of three different elements, i.e., phosphorus, nitrogen, and oxygen, in almost linear fashion. By using pyphos ligand, linearly aligned tetrametal complexes of group 10 metals $[Mo_2M_2(pyphos)_4X_{2n}]$ (M = Pt and Pd; $n = 0$, 1, and 2) were prepared, and for group 9 metals, $[Mo_2M_2(pyphos)_4(RNC)_4X_{2n}]^{2+}$ (M = Ir and Rh; $n = 0$ and 1). Fully metal-to-metal bonded complexes were obtained by reduction of M^{II} to M^{I} for group 10 metals and by oxidation of M^{I} to M^{II} for group 9 metals. Both reactions afforded complexes having unique M–Mo≡Mo–M skeletons, i.e., metalla-2-butyne. Structural and chemical properties were systematically investigated for M^0 (M = Pt and Pd) and M^I (M = Ir and Rh). Thus, oxidative reactions of Pd^0 complexes $[Mo_2Pd_2(pyphos)_4]$ and Ir^I complexes $[Mo_2Ir_2(pyphos)_4(RNC)_4]^{2+}$ with RX or X_2 were studied and unique 1,4-addition reaction was demonstrated. Dichromium complexes analogous to dimolybdenum complexes were prepared and axial donation of $PtMe_2$ moiety significantly elongated the Cr–Cr bond, due to the dative bonding interaction between Cr^{II} and Pt^{II} units.

1. Introduction

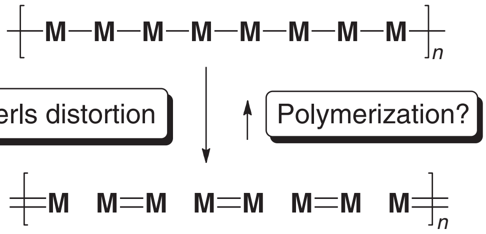
Direct bonding interaction among metal atoms, in particular, multiply-bonded dinuclear complexes including the most characteristic concept of δ bonding, has been intensively studied over the last decades as one of the most attractive targets in inorganic chemistry.[1] As a resemblance to carbon-to-carbon double and triple bonds, an ideal reaction leading to one-dimensional metal complexes bearing metal–metal bonds, which have attracted much interest in terms of not only bonding nature[1] but also potential applications as single-molecule transistors,[2–4] (semi)conductors,[5] and so on, is polymerization of such multiply-bonded dinuclear complexes. However, it has been known that the aligned metal array in principle turns to the assembly of dinuclear metal units due to the Peierls distortion (Scheme 1). In addition, it is necessary to avoid the perpendicular alignment of multiply-bonded dinuclear units and the [2 + 2] cyclodimerization of multiply-bonded dinuclear complexes of Re,[6,7] Mo,[8–12] and W[13] (eq 1).



(1)

Many efforts have been devoted to construct nanometer-scale metal strings connected entirely by metal–metal bonds. Three synthetic approaches have been rationally conducted for one-dimensional homoleptic and heteroleptic transition-metal clusters with more than three metal ions; thus categorized as (1) use of non-bridged mixed valent metal complexes like platinum blue species, (2) use of suitable multidentate ligands for lapping the metal strings, and (3) use of dative bond or strong closed-shell interactions among heavier metal ions with d^8, d^{10}, and s^2 configurations.

1.1 Homoleptic Linear Transition-Metal Clusters. A typical example of category (1) is the partially oxidized tetracyanoplatinate salts $\{K_2[PtBr_{0.3}(CN)_4]\cdot3H_2O\}_\infty$, referred to as Krogmann salts, which were reported to have unique short Pt⋯Pt bonding interactions through overlapping the d_{z^2} orbital of each platinum atom.[14] In the same manner, controlled-potential electrolysis afforded one-dimensional materials:



Scheme 1. One-dimensional materials vs. multiply-bonded dinuclear complexes.

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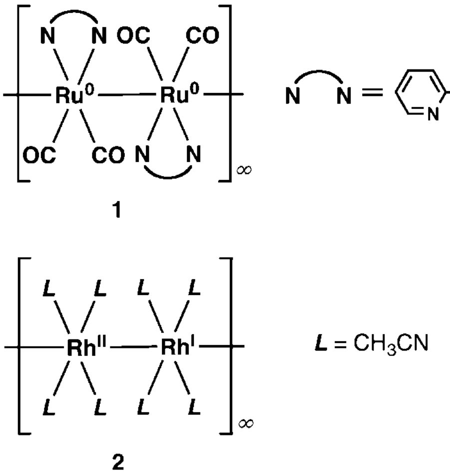
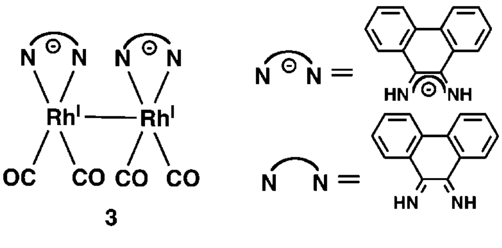
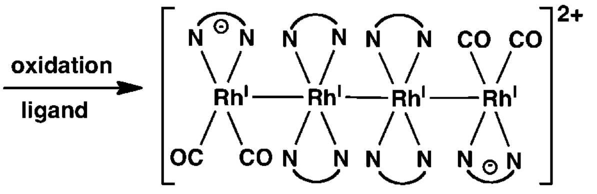


Chart 1.

Ziessel et al. synthesized a deep blue film of $[\mathrm{Ru}^0(\mathrm{bpy})(\mathrm{CO})_2]_\infty$ (**1**) (bpy = 2,2′-bipyridine) on a working electrode from *trans*-$[\mathrm{Ru}^{\mathrm{II}}(\mathrm{bpy})(\mathrm{CO})_2\mathrm{Cl}_2]$,[15,16] and Dunbar et al. prepared a 1D rhodium chain, $\{[\mathrm{Rh}(\mathrm{CH_3CN})_4][\mathrm{BF_4}]_{1.5}\}_\infty$ (**2**) (Chart 1), as crystalline solids from electrochemical reduction of $[\mathrm{Rh_2}^{\mathrm{II,II}}(\mathrm{MeCN})_{10}][\mathrm{BF_4}]_4$ at a Pt electrode, in which there were bonding interactions among $\mathrm{Rh^I}$ and $\mathrm{Rh^{II}}$ atoms with two different contacts.[17] A similar strategy has been utilized for dimerization of dinuclear complexes: a tetrarhodium complex, $[\mathrm{Rh^I}_4(\mathrm{CO})_4(\mathrm{pqdi})_4(\mathrm{s\text{-}pqdi})_2]^{2+}$ (**4**) (s-pqdi = 9,10-phenanthrosemiquinone diimine; pqdi = 9,10-phenanthroquinone diimine), was prepared by the oxidative dimerization of the dirhodium complex of $[\mathrm{Rh^I}(\mathrm{CO})_2(\mathrm{s\text{-}pqdi})]_2$ (**3**) (eq 2).[18] Mixed-valent oligomers of platinum,[19–21] rhodium,[22] and iridium[23] were also reported. Another synthetic method was mixing transition-metal complexes with different oxidation states: the reaction of a dipalladium(I) isonitrile complex, $[\mathrm{Pd_2}(\mathrm{CH_3NC})_6]^{2+}$, with a monopalladium(0) complex, $[\mathrm{Pd}(\mathrm{CH_3NC})_x]$, resulted in the selective formation of a mixed-valent linear homotrinuclear $\mathrm{Pd_3}$ complex, $[\mathrm{Pd_3}(\mathrm{CH_3NC})_8]^{2+}$.[24]





(2)

4

In category (2), an approach for constructing one-dimensional materials comprised of multiply-bonded dinuclear units using appropriate supporting ligands was studied by Chisholm and his co-workers.[25] They connected two quadruply-bonded $\mathrm{Mo_2}$ units by a chelating ligand, the dianion of 2,7-dihydroxynaphthyridine, to give a dimer compound **5** with no direct bonding interaction between the inner Mo atoms, and an assembled paddle-wheel or lantern-type $\mathrm{M_2(O_2CR)_4}$ core with long alkyl chain in the absence of neutral donor ligands to give liquid crystalline laddered complexes **6**, both complexes bearing an intermolecular oxygen-to-metal interaction (Chart 2).

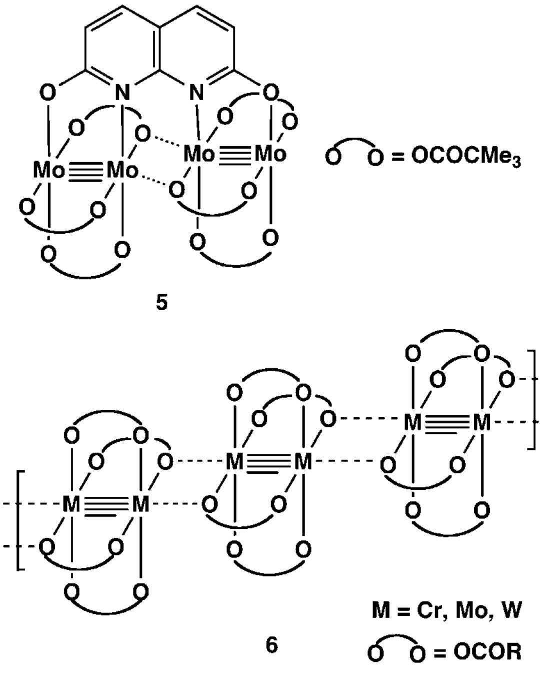


Chart 2.

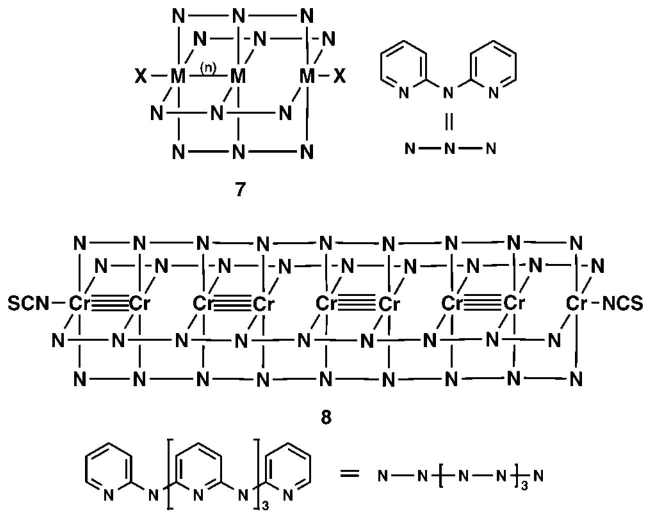
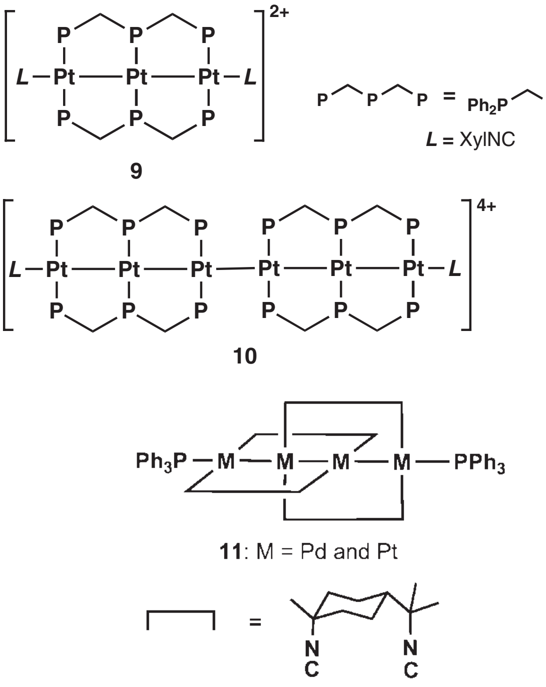


Chart 3.

Multidentate ligands have played an important role in preparing homoleptic one-dimensional transition-metal complexes.[26] Linearly aligned $\mathrm{Ni_3}$ and $\mathrm{Cu_3}$ complexes $[\mathrm{M_3(dpa)_4X_2}]$ (**7**) (dpa = di(2-pyridyl)amide) were reported by Hathaway[27] and Pyrka.[28] Later, two independent groups of Peng and Cotton intensively investigated the same type of homoleptic linear trinuclear $\mathrm{M_3}$ complexes **7** (M = Cu, Co, Ni, Cr, Ru, Rh, and so on) using dpa and related multidentate ligands (Chart 3).[29–32] These complexes were crystallographi-



9

L = XylNC

10

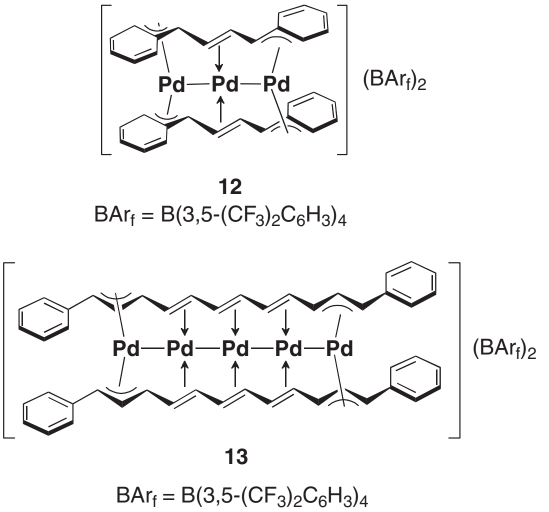
11: M = Pd and Pt

Chart 4.

cally characterized, and some of them are an assembly of a dimer unit and a mononuclear unit; however, chemical oxidation induced the bond formation through all three metals. Peng and Cotton have also developed this line of chemistry to much longer metal oligomers by using oligo(α-pyridyl)-amido ligands as well as their analogs, synthesizing tetra-,[33] penta-,[34–42] hexa-,[43,44] hepta-,[45,46] octa-,[47] and nonanuclear chain[48,49] of various metal atoms. Among them, a linear nona-chromium complex $[Cr_9(\mu_9\text{-}N_9\text{-mpz})_4(NCS)_2]$ (**8**) (N_9-mpz = N,N'-bis[6-(2-pyridylamino)-2-pyridyl]pyrazine-2,6-diaminato) is schematically drawn.[48]

Bis(diphenylphosphinomethyl)phenylphosphine (dpmp) is a triphosphine ligand that is able to support three metals in a linear fashion. In fact, $[Pt_3(dpmp)_2(XylNC)_2](PF_6)_2$ (**9**) (XylNC = 2,6-dimethylphenyl isocyanide) was prepared (Chart 4),[50] and complex **9** was converted by excess $NaBH_4$ to a hydride-bridged dimer $[Pt_6(\mu\text{-}H)(dpmp)_4(XylNC)_2]^{3+}$ and then followed by chemical oxidation to give the dimer of **9**, $[Pt_6(dpmp)_4(XylNC)_2]^{4+}$ (**10**).[51] A hetero-tridentate P–As–P ligand, bis(diphenylphosphinomethyl)phenylarsine (bdppa), was used to prepare a tetranuclear Au_4 complex, $[Au_4Cl_2(bdppa)_2]^{2+}$.[52] Bridging bis(isocyanide) ligands, 1,3-diisocyanopropane (dpb) and 1,8-diisocyano-p-menthane (dmb), yielded a tetrarhodium complex, $[Rh_4Cl(dpb)_8]^{5+}$,[53–55] and tetraplatinum and tetrapalladium compounds $[M_4(dmb)_4(PPh_3)_2]Cl_2$ (**11**: M = Pd and Pt).[56]

Conjugated polyenes and aromatic compounds acted as supporting ligands of multinuclear palladium complexes. Murahashi and Kurosawa reported that the combination of Pd^0 and Pd^{II} precursors in the required ratio in the presence of conjugated polyenes afforded multinuclear mixed-valent palladium complexes **12** and **13** (Chart 5), which had entirely Pd–Pd bonds through the arrays, and conjugated aromatic compounds produced linear or planar palladium clusters.[57]



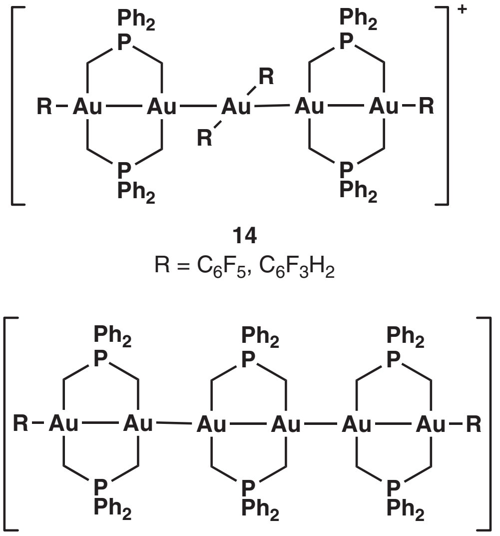
12

$BAr_f = B(3,5\text{-}(CF_3)_2C_6H_3)_4$

13

$BAr_f = B(3,5\text{-}(CF_3)_2C_6H_3)_4$

Chart 5.



14

$R = C_6F_5, C_6F_3H_2$

15

$R = C_6F_5, C_6F_3H_2$

Chart 6.

The third category is based on the metallophilic interaction, where two closed-shell heavy late transition metals with d^8 and d^{10} configurations have an attracting bonding interaction.[58] Such bonding interaction has been successfully used for forming a linearly aligned mixed-valent pentanuclear Au_5 complex $[\{RAu(CH_2PPh_2CH_2)_2Au\}_2AuR_2]ClO_4$ (**14**) and a hexanuclear Au_6 complex, $[\{RAu(CH_2PPh_2CH_2)_2Au\}_2\{Au(CH_2PPh_2CH_2)_2Au\}](ClO_4)_2$ (**15**) ($R = C_6F_5$ and $C_6F_3H_2$) (Chart 6).[59]

1.2 Heteroleptic Linear Transition-Metal Clusters. For the synthesis of linear hetero-multinuclear complexes of more than three metal atoms, a few non-bridged hetero multi-metal complexes have been reported. Yamaguchi and Ito prepared a linear pentanuclear complex, $[\{Pt(thpy)_2\}\{Ag(acetone)\}]_n[ClO_4]_n$ (thpy = the anion of 2-(2-thienyl)pyridine), and an infinite helical compound, $[\{Pt(phpy)_2\}\{Ag(acetone)\}]_n[ClO_4]_n$ (phpy = the anion of 2-phenylpyridine), both of which had a sequence of Pt and Ag and were connected by a Pt → Ag

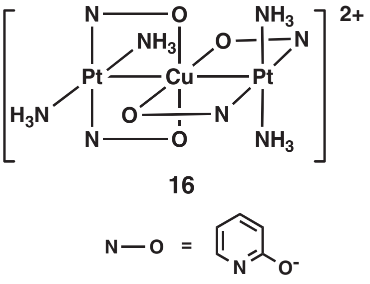
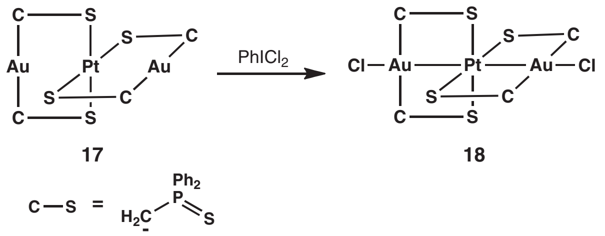


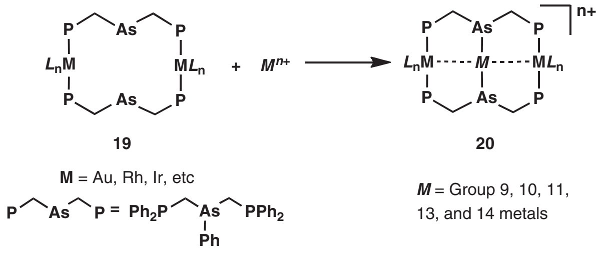
Chart 7.

dative bond.[60] In sharp contrast, many research work has been investigated by appropriate multidentate ligands containing different elements as coordination sites for supporting two different kinds of metals (category 2). Pyridonato ligand and its derivatives have been applied to form a heterotrinuclear Pt_2Cu complex, *trans*-$[(NH_3)_2Pt(C_5H_4NO)_2Cu(C_5H_4NO)_2Pt(NH_3)_2]^{2+}$ (**16**) (Chart 7),[61] along with some related trinuclear Pt_2M complexes.[62] By using $[CH_2P(S)Ph_2]^-$ (mtp), a linear trinuclear complex, $[Au_2Pt(mtp)_4]$ (**17**), was formed. Chemical oxidation of **17** produced a chlorinated complex, $[Au_2PtCl_2(mtp)_4]$ (**18**) (eq 3).[63] A similar heterotrinuclear complex $[Au_2Pb(mtp)_4]$ was also reported.[64]



(3)

Balch and his co-workers used a tridentate ligand, bis(diphenylphosphinomethyl)phenylarsine (bdppa), forming macrocycles **19** comprised of two metal ions in their ring system, and then added various metal ions to give heterotrinuclear M_2M'-type complexes **20** (eq 4), where $M_2M' = Au_2Rh$ ($d^{10}d^8d^{10}$), Au_2Ir ($d^{10}d^8d^{10}$), Rh_2Au ($d^8d^{10}d^8$), Ir_2Au ($d^8d^{10}d^8$), Ir_2Ag ($d^8d^{10}d^8$), and so on,[65] where closed-shell interaction is a key attracting force.



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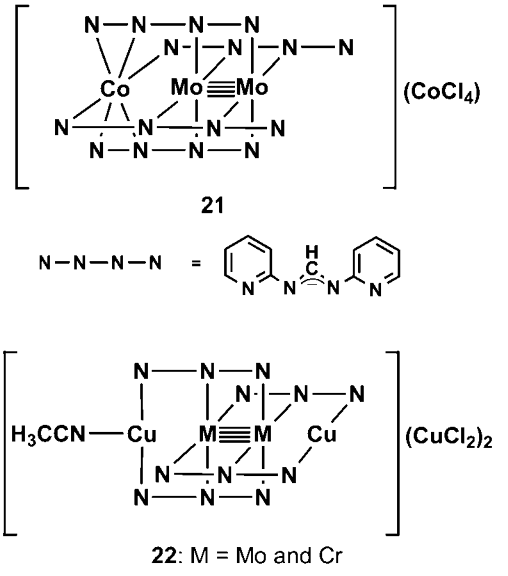


Chart 8.

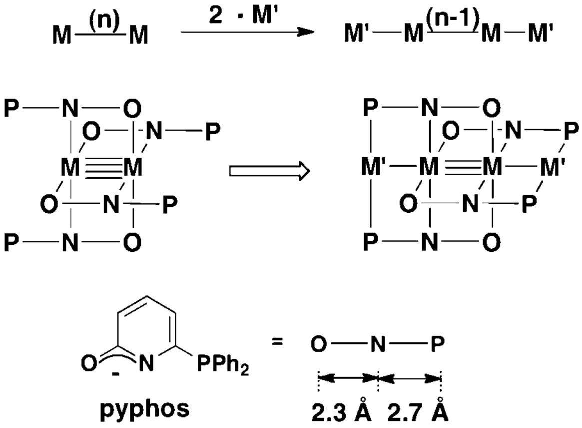


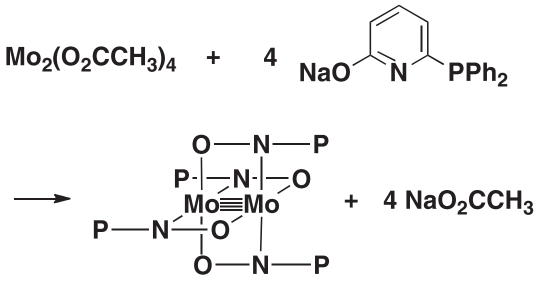
Figure 1. Strategy to synthesize a linear tetranuclear complex, metalla-2-butyne, as decreasing bond order of multiple bond of M_2 and forming new M–M′ single bonds.

Concerning the strategy depicted in Scheme 1, synthetic studies of linear heteroleptic complexes bearing multiply-bonded dinuclear units have not been well-developed yet. By using di(2-pyridyl)formamidinate (dpyf), heteronuclear $[Mo_2Co(dpyf)_4][CoCl_4]$ (**21**) was obtained (Chart 8),[66] and the use of the anion of 2,6-di(phenylimino)piperidine (dPhip) resulted in the formation of a tetranuclear complex $[M_2Cu_2(dPhip)_4(CH_3CN)][CuCl_2]_2$ (**22**: M = Cr and Mo), in which the Cu atoms have only weak interactions with the M atoms.[32] We have focused our attention on synthesizing heterometallic tetrametal complexes with the multiply-bonded unit in an array and elucidating their fundamental chemical properties. We have thus chosen a tridentate ligand, Hpyphos (6-diphenylphosphino-2-pyridone), because this has unique coordinating sites comprised of three elements, i.e., phosphorus, nitrogen, and oxygen, in almost linear fashion. The most attractive aspect of our synthetic strategy is illustrated in the reaction outlined schematically in Figure 1, where the addition of two unpaired transition metals M′ to the multiply-bonded M_2 moiety generated new tetrametal compounds with decrease of bond-multiplicity at the central M_2 and the formation of M–M′ bonds. This account discloses unique tetranuclear complexes bearing a skeleton of M′–M–M–M′, where M are molybdenum and chromium and M′ are group 9 and 10 metals, by using tridentate pyphos (6-diphenylphosphino-2-pyridonato) ligand.

2. Synthesis of Dinuclear Complexes Supported by pyphos Ligands

Based on the soft–hard combination of elements of the pyphos ligand with metals, the pyridone served as a supporting ligand of multiply-bonded dinuclear moieties, while the phosphine favorably coordinated to late transition metals, leading to heterotetrametal complexes (Figure 1). Furthermore, the P–N bridge has a suitable distance to support the single bond between transition metals, and the N–O bridge is best fit to a shorter multiple bond such as a quadruple bond in the dinuclear complexes of group 6 metals. In fact, the N–O coordination of mhp ligand (mhp = the anion of 2-hydroxy-6-methylpyridine) was utilized for supporting quadruply-bonded dinuclear complexes of chromium, molybdenum, and tungsten.[67–69] A typical N–P bridging ligand, 2-(diphenylphosphino)pyridine, coordinates to later transition metal atoms such as rhodium, palladium, and platinum to form dinuclear complexes with rather long metal-to-metal distances.[70]

At first, we prepared the dinuclear molybdenum complex **23** by treating $Mo_2(OAc)_4$ with the sodium salt of the pyphos ligand. Complex **23** has four pyphos ligands for supporting a quadruple Mo–Mo bond and two axial positions are suitable for the coordination of two soft, late transition metals (eq 5).

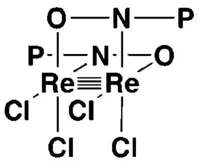


(5)

23

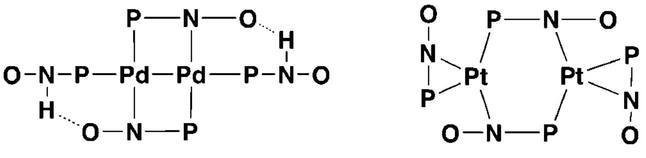
Similarly, reaction of $[Re_2Cl_8]^{2-}$ with an excess amount of Hpyphos in refluxing acetonitrile solution afforded $[Re_2Cl_4(\text{pyphos})_2]$ (**24**) (Chart 9), whose Re–Re bond was determined by X-ray analysis to be a quadruple bond.[71]

In contrast, treatment of pyphos ligand with palladium and platinum precursors resulted in the formation of two dinuclear complexes of palladium(I) $[Pd_2(\text{Hpyphos})_2(\text{pyphos})_2]$ (**25**), which has a Pd–Pd single bond surrounded by two pyphos ligands and two Hpyphos ligands, and platinum(II), $[Pt_2(\text{pyphos})_4]$ (**26**), which has no metal–metal bond (Chart 10).[72] Our tridentate ligand mainly coordinated by its phosphorus moiety to a ruthenium(II) center.[73]



24

Chart 9.



25 **26**

Chart 10.

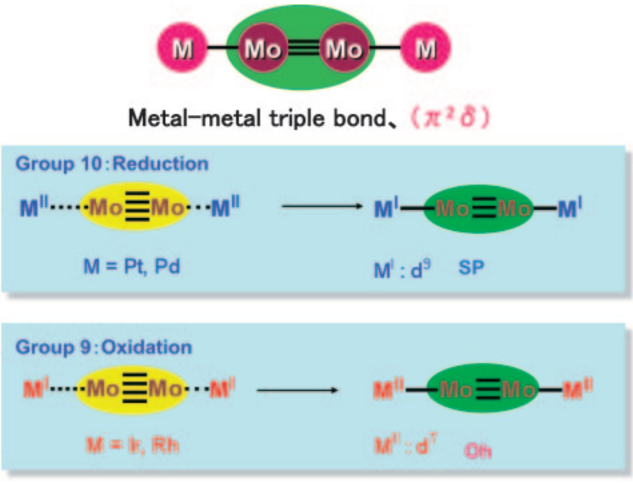


Figure 2. Synthetic strategies for tetrametal cluster with a new triple bond.

3. Synthesis and Chemical Properties of Tetranuclear M–Mo–Mo–M Complexes

Using the complex **23** as a starting material, we prepared two types of tetrametal complexes Mo_2M_2 (M = Pt and Pd) and Mo_2M_2 (M = Ir and Rh). For group 10 metals, reduction of M^{II} to M^{I} afforded fully metal–metal bonded tetrametal complexes, while oxidation of group 9 metals from M^{I} to M^{II} resulted in the formation of the corresponding tetrametal complexes as schematically described in Figure 2. Of interest, both products have the triply-bonded Mo_2 core of $(\pi^2\delta)$ component, being in sharp contrast to $(\sigma\pi^2)$ component of the carbon–carbon triple bond.

3.1 Mo_2M_2 (M = Pt and Pd) Complexes. Linearly aligned tetrametal complexes $[Mo_2Pt_2(\text{pyphos})_4X_2]$ (**29**) (**a**: X = Cl, **b**: X = Br, and **c**: X = I) and $[Mo_2Pd_2(\text{pyphos})_4X_2]$ (**30**) (**a**: X = Cl, **b**: X = Br, and **c**: X = I) have fully metal-to-metal bonded fragments of M–Mo≡Mo–M (M = Pt and Pd) supported by four pyphos ligands (eq 6).[74,75] As the first step of preparing **29** and **30**, the corresponding M^{II} tetranuclear complexes, $[Mo_2M_2(\text{pyphos})_4X_4]$ (M = Pt (**27**), Pd (**28**); **a**: X = Cl, **b**: X = Br, and **c**: X = I), were prepared. These complexes **27** and **28** have two d^8 group 10 metals in the line of the axial vector of the Mo–Mo unit; however, there were no bonding interaction of two metal ions with the quadruply-bonded Mo_2 and the square planes of two group 10 ions were perpendicular to the vector of the Mo_2 core. Chemical, thermal, or irradiative reduction of **27** and **28** afforded the corresponding complexes **29** and **30**, in which each metal ion interacts with a molybdenum atom

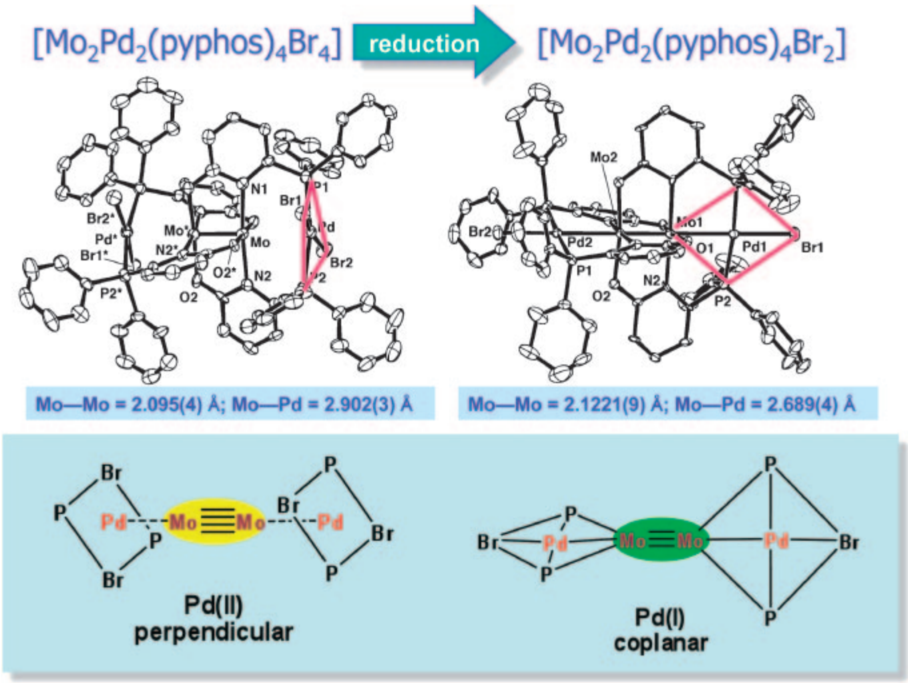
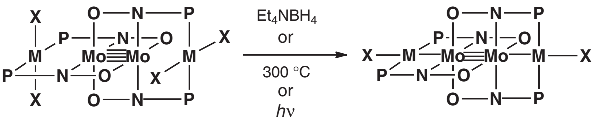


Figure 3. Schematically equation for reductive formation of a Pd–Mo≡Mo–Pd complex **30b** from **28b**.

to significantly elongate the Mo–Mo distance and the molybdenum atom occupies one corner of the square planer of each metal ions (Figure 3). Entirely metal-to-metal bonded tetrametal complexes with longer conjugated systems show third-order nonlinear optical properties.[76,77] Such reductive transformation was not observed for trinuclear $[Mo_2Pt(OCOR)_2(pyphos)_2X_2]$.[78]



(6)

27: M = Pt
28: M = Pd
a: X = Cl
b: X = Br
c: X = I

29: M = Pt
30: M = Pd
a: X = Cl
b: X = Br
c: X = I

We tried two approaches for assembling tetrametal units by alkyne coupling and coordination polymerization. We introduced alkyne groups at both of the axial positions of a linear Mo_2Pt_2 fragment: an acetylide complex, $[Mo_2Pt_2(C\equiv CSiMe_3)_2(pyphos)_4]$ (**31**), was prepared by treating $[Mo_2Pt_2Cl_2(pyphos)_4]$ (**29a**) with two equivalents of lithium trimethylsilylacetylide (eq 7).[79] Desilylation followed by spontaneous oxidation coupling gave solid, which was assumed to be a poly(yne) polymer containing a Mo_2Pt_2 moiety in its backbone, though its characterization was hampered by its low solubility.[79] Recently, Ren reported that bis(ferrocenylethynyl) dinuclear complexes containing a Ru_2 unit showed significant electronic couplings of ferrocenyl moieties through the Ru_2 unit.[80] Reaction of the lithium salt of 1-ferrocenylacetylene with $[Co_3(dpa)_4(NCCH_3)_2][PF_6]_2$ afforded the bis-ferrocenylacetylide derivative bearing a $Co_3(dpa)_4$ fragment,[81] and its triruthenium derivative also was reported.[82]

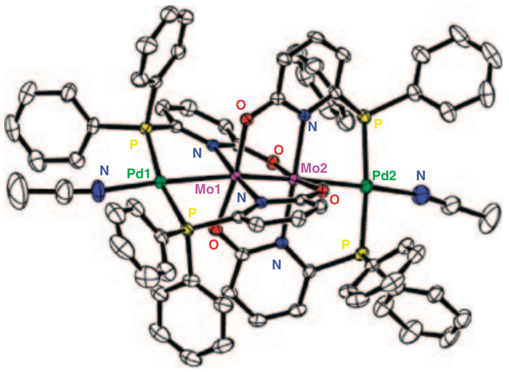
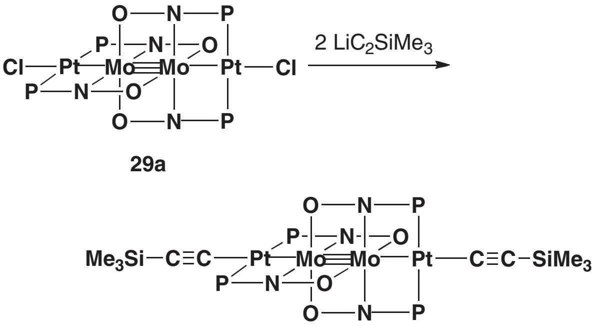


Figure 4. Crystal stucture of $[Mo_2Pd_2(pyphos)_4(NCCH_3)_2]^{2+}$ (**32**).

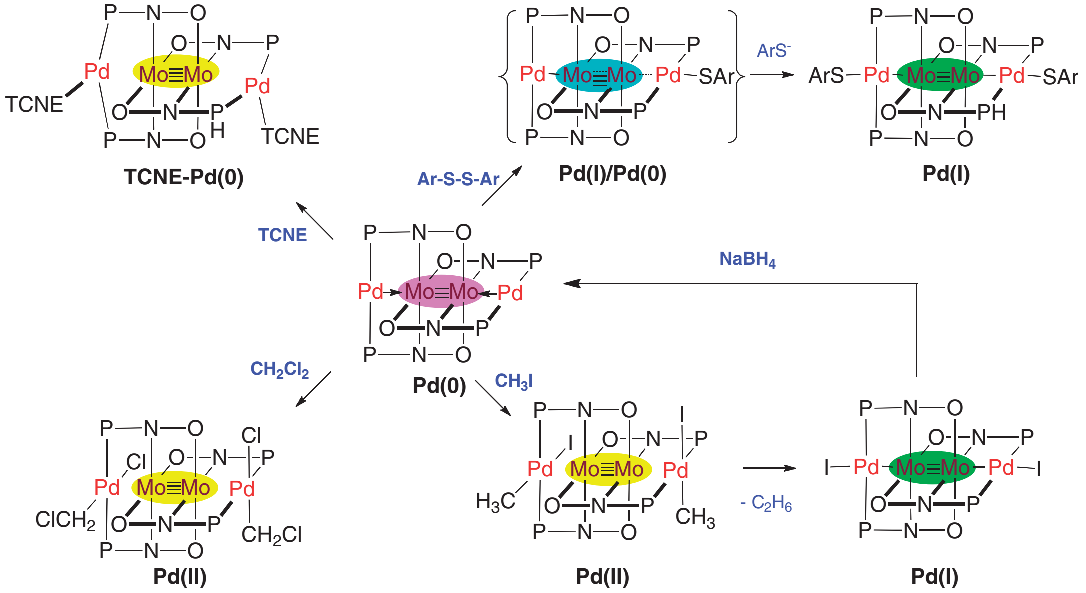


(7)

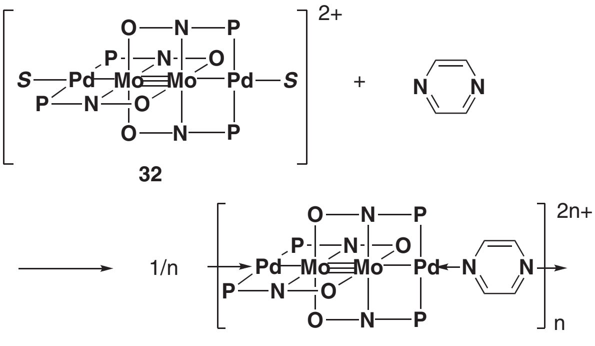
29a

31

The second approach was the coordination polymerization of a dicationic complex, $[Mo_2Pd_2(pyphos)_4(NCCH_3)_2]^{2+}$ (**32**), whose crystal structure is depicted in Figure 4, with a bidentate ligand, pyrazine (=pyz), to give $[Mo_2Pd_2(pyphos)_4(pyz)]_n[BF_4]_{2n}$ (**33**) (eq 8).[79]



Scheme 2. Some reactions of $[Mo_2Pd_2(pyphos)_4]$ (**34**).



32

(8)

33

It was to our surprise that coordinatively unsaturated Pd^0 tetrametal complex, $[Mo_2Pd_2(pyphos)_4]$ (**34**), could be obtained by treating $[Mo_2Pd_2(pyphos)_4X_2]$ (**30**) with appropriate alkylating reagents, in sharp contrast to the successful isolation of the alkynyl derivative. Alternatively, complex **34** was obtained in high yield by the reaction of $[Mo_2(pyphos)_4]$ (**23**) with a Pd^0 source such as $[Pd(dba)_2]$ (dba = dibenzylideneacetone).[83] Once isolated, such coordinatively unsaturated Pd^0 complex was found to be rather stable due to the presence of $Pd^0 \rightarrow Mo^{II}$ dative bonds. Since there were two zero-valent palladium atoms at both axial positions of a quadruply-bonded Mo_2 core of **34**, some typical reactivities due to the Pd^0 species were observed. The reaction of **34** with various π-ligands (L) such as olefins, alkyne, isocyanides, carbon monoxide, and phosphine afforded the corresponding adducts, $[Mo_2Pd_2(L)_2(pyphos)_4]$ (**35**) (**a**: L = acrylonitrile, **b**: L = fumaronitrile, **c**: L = tetracyanoethylene (=tcne), **d**: L = diisopropyl fumarate, **e**: L = diethyl fumarate, **f**: L = dimethyl fumarate, **g**: L = dimethyl maleate, **h**: L = 2,6-xylyl isocyanide, **i**: L = *tert*-butyl isocyanide, **j**: L = dimethyl acetylenedicarboxylate, **k**: L = 1,4-benzoquinone, **l**: L = 1,4-naphthoquinone, **m**: L = carbon monooxide, and **n**: L = triphenylphosphine) (Scheme 2 and Figure 5).[83,84] Similar Pt^0 complexes coordinated by phosphine and phosphite have been obtained.[85]

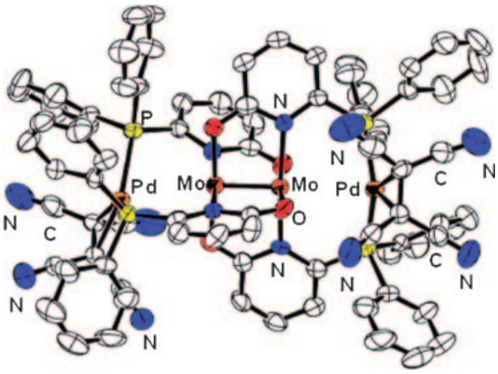
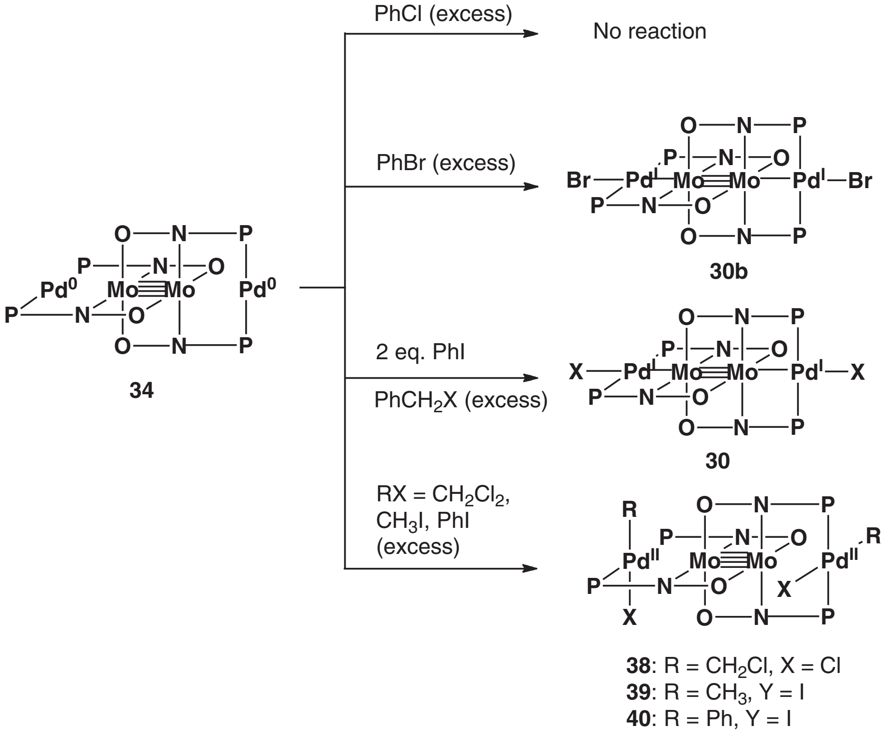


Figure 5. Crystal structure of $[Mo_2Pd_2(pyphos)_4(tcne)_2]$ (**35c**).

We examined oxidative addition reactions of **34**.[83,84] Disulfides and benzoyl peroxide added in a 1,4-fashion to the Pd^0 centers of **34** to give the corresponding Pd^I complexes $[Mo_2Pd_2(pyphos)_4(SAr)_2]$ (**36**: Ar = C_6H_5, 4-$Me_3CC_6H_4$, 4-MeC_6H_4, and 4-$NO_2C_6H_4$) and $[Mo_2Pd_2(OCOPh)_2(pyphos)_4]$ (**37**), respectively (Scheme 2). The reactions of alkyl and aryl halides to **34** gave rise to two different reaction patterns: excess amounts of benzyl halides BnX (X = Cl, Br, and I), PhCl, and PhBr, and 2 equiv of PhI reacted with **34** to give Pd^I complexes $[Mo_2Pd_2(pyphos)_4X_2]$ (**30**). The most notable reactivity was that the Pd^0 atom surrounded by two phosphine atoms and one molybdenum exhibited unexpected high reactivity toward CH_2Cl_2, resulting in the isolation of double oxidative addition product of Pd^{II}, $[Mo_2\{PdCl(CH_2Cl)\}_2(pyphos)_4]$ (**38**) (Scheme 2 and Figure 6), in contrast to oxidative reaction of a dinuclear Pd^0 complex, $[Pd_2(\mu\text{-dppm})_3]$ [dppm = bis(diphenylphosphino)methane], with CH_2Cl_2 resulted in a A-shape dinuclear Pd^{II} product having a bridged methylene group.[86] The reactions of **34** with excess amounts of CH_3I and PhI also afforded similar Pd^{II} complexes, $[Mo_2\{Pd(CH_3)I\}_2(pyphos)_4]$ (**39**) and $[Mo_2\{Pd(Ph)I\}_2(pyphos)_4]$ (**40**), respectively (Schemes 2 and 3).



Scheme 3. Reactions of **34** with alkyl and aryl halides.

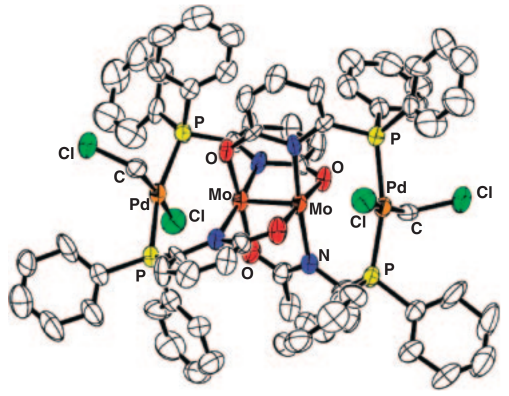
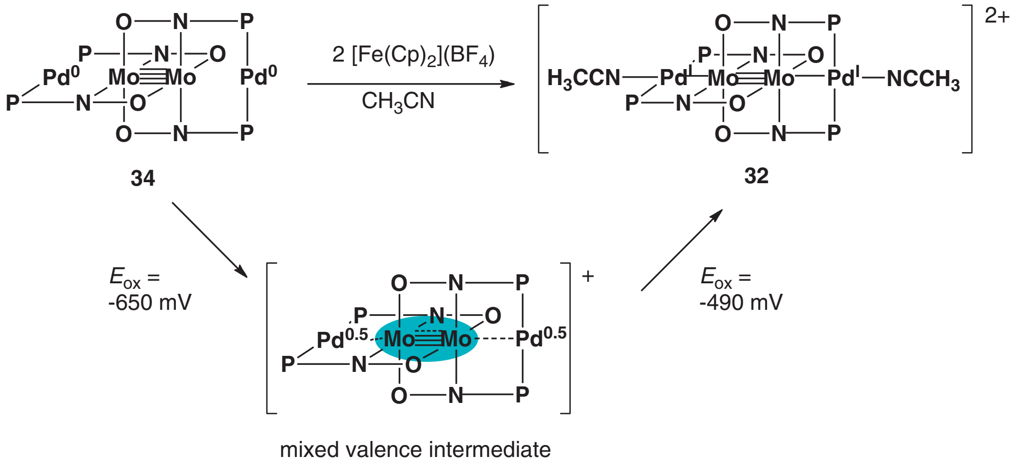


Figure 6. Crystal structure of $[Mo_2\{PdCl(CH_2Cl)\}_2(pyphos)_4]$ (**38**).

It was still difficult to explain such unique reaction modes with oxidants; however we were able to measure the electrochemical characteristics of **34**. Cyclic voltammetry of **34** in acetonitrile and THF displayed two reversible waves at −490 and −650 mV vs. Ag/Ag^+ ($\Delta E_{1/2} = 160$ mV) in acetonitrile and −200 and −415 mV vs. Ag/Ag^+ ($\Delta E_{1/2} = 215$ mV) in THF, the electrochemical properties depending on the solvent due to the coordination of solvent molecules to the Pd^I species during oxidation. Thus, it was reasonably assumed that the first one-electron oxidation of **34** gave a mixed-valence monocationic species $[\mathbf{34}]^+$, where two palladium atoms electrochemically communicated through a Mo_2 unit, and the second one-electron oxidation resulted in the formation of $[\mathbf{34}]^{2+}$, i.e., complex **32** in acetonitrile (Scheme 4). Chemical oxidation of **34** with 2 equiv of $[Fe(Cp)_2][BF_4]$ in other donor molecules afforded dicationic Pd^I complexes $[Mo_2Pd_2(L')_2(pyphos)_4][BF_4]_2$ [L′ = acetonitrile (**32**), dimethyl sulfoxide, THF, benzonitrile, *p*-methoxybenzonitrile, *p*-trifluoromethylbenzonitrile, pyridine, and *p*-(dimethylamino)pyridine], suggesting that there was an attractive bonding interaction between a closed-shell d^{10} Pd^0 with Mo_2 core. Such solvent effect is consistent with the known evidence that the metal–metal bonding nature of paddle–wheel-type dinuclear complexes are sensitive to axial ligands.[87] Chemical oxidation of Pt^0 complexes, $[Mo_2Pt_2(PR_3)_2(pyphos)_4]$, also proceeded in a stepwise manner.[85] Referring to such bonding interaction, it should be pointed out that there are d^{10} closed shell dinuclear palladium complexes, $[Pd_2(\mu\text{-dppm})_3]$,[88,89] $[Pd_2(\mu\text{-dmpm})_3]$ [dmpm = bis(dimethylphosphino)methane],[90] $[Pd_2(\mu\text{-MeN-}\{P(OPh)_2\}_2)_3]$,[91] $[Pd_2(\mu\text{-dafo})\{1,4\text{-}C_6H_4(=O)_2\}_2]$ (dafo = 4,5-diazafluorene-9-one),[92] and $[Pd_2\{\mu\text{-}CH_2(PR_2)_2\}_2]$ (R = ^{i}Pr and *c*-C_6H_{11}),[93,94] which have been reported to have unique attractive bonding interaction between two Pd^0 atoms through d–p mixed σ-bonding orbitals.

3.2 Mo_2M_2 (M = Ir and Rh) Complexes. Other linear hetero tetrametallic Mo_2M_2 (M = Ir^I and Rh^I) complexes were prepared and their unique oxidative reactions to form metal–metal bonding in metal arrays were studied. Reaction of $[Mo_2(pyphos)_4]$ (**34**) with $[M_2(CO)_4Cl_2]$ (M = Ir and Rh) gave linear tetranuclear complexes of the formula, $[Mo_2M_2(CO)_2Cl_2(pyphos)_4]$ (**41**: M = Ir and **42**: M = Rh), which were further treated by ^{t}BuNC and XylNC to yield the corresponding dicationic complexes $[Mo_2M_2(pyphos)_4(^tBuNC)_4]Cl_2$ (**43a**: M = Ir and **44a**: M = Rh) and $[Mo_2Ir_2(pyphos)_4(XylNC)_4]Cl_2$ (**43b**: M = Ir and **44b**: M = Rh) with the release of CO (eq 9). Crystallographic studies of Mo_2M_2 complexes **41**–**44** confirmed that there was no direct σ bonding interaction between M^I atoms and the Mo_2 core.[95,96]



Scheme 4. Stepwise oxidation of $[Mo_2Pd^0_2(pyphos)_4]$ (**34**) through a mixed-valence intermediate.

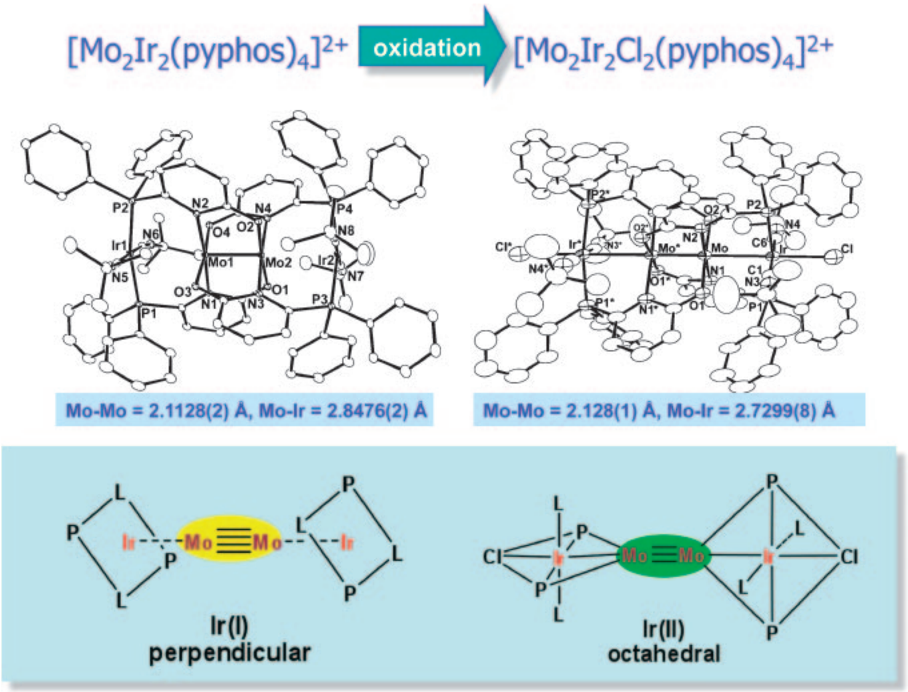
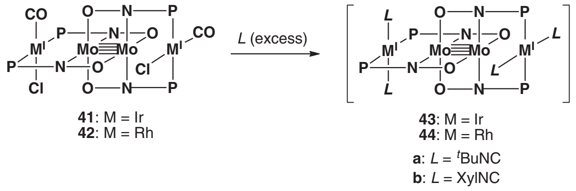
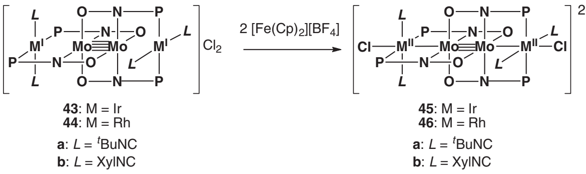


Figure 7. Schematically equation for oxidative formation of a Ir–Mo≡Mo–Ir complex **45a** from **43a**.



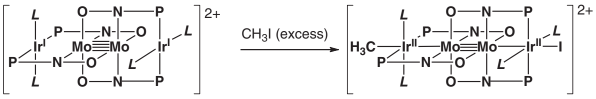
(9)

Oxidation of these complexes by either two equiv of $[Fe(Cp)_2][PF_6]$ or excess I_2 afforded the corresponding M^{II} complexes, $[Mo_2M_2(L)_4(pyphos)_4X_2]^{2+}$ (**45**: M = Ir and **46**: M = Rh; **a**: L = ^{t}BuNC and **b**: L = XylNC; X = Cl, Br, and I) (eq 10), in which the bond order of the Mo–Mo moiety decreased to three as shown in Figure 7. It is obvious that the square plane around the M^I (M = Ir and Rh) fragments supported by $[Mo_2(pyphos)_4]$ system is perpendicular to the Mo–Mo vector, and hence the contribution of the direct σ-bonding interaction between the two M^I atoms and the Mo_2 cores in these tetranuclear complexes is neglected, though its distance was not as long as found for the Pd^{II} complexes $[Mo_2Pd_2(pyphos)_4X_4]$ (**28**). Chemical oxidation of both group 9 metals M^I (M = Ir and Rh) to M^{II} spontaneously proceeded with the formation of M–Mo bonds and decreased the bond order of the Mo_2 moiety. The resulting M^{II} ions favorably adopted octahedral geometry, in which one corner of each M^{II} ion was occupied by a Mo atom.



(10)

Some alkyl halides oxidatively reacted with the Ir^I complexes **43a** and **43b** to give unique 1,4-oxidative addition products, while the corresponding rhodium complexes **44a** and **44b** did not react under the same conditions. Reaction of the Ir^I complexes **43a** and **43b** with CH_3I afforded unique "1,4-oxidative addition" products of methyl iodide, $[Mo_2Ir_2(CH_3)(^tBuNC)_4I(pyphos)_4]Cl_2$ (**47a**) and $[Mo_2Ir_2(CH_3)(XylNC)_4I(pyphos)_4]Cl_2$ (**47b**), respectively (eq 11). It was of interest that there were no homo-substituted Ir^{II} products, such as diiodo and dimethyl complexes. Similar 1,4-oxidative addition product $[Mo_2Ir_2(CH_2Cl)(^tBuNC)_4Cl(pyphos)_4]Cl_2$ (**48**) was obtained in the reaction of dichloromethane with **43a**. Kinetic analysis of the reaction of **43a** with CH_3I suggested that the 1,4-oxidative addition to the Ir^I complex proceeded by a S_N2 reaction mechanism. Similarly, oxidative addition of diaryl disulfides afforded bis(thiolato) Ir^{II} complexes $[Mo_2Ir_2(^tBuNC)_4(pyphos)_4(SAr)_2]Cl_2$, in accord with the 1,4-oxidative addition to Pd^0 complex.



(11)

43
a: *L* = ^{t}BuNC
b: *L* = XylNC

47
a: *L* = ^{t}BuNC
b: *L* = XylNC

Cyclic voltammogram of the Mo_2Ir_2 complex **45a** measured in TBACl/MeCN solution at room temperature with a positively-directed sweep showed a reversible, two-electron wave at −970 mV (vs. Fc/Fc^+), which was determined to be an $Ir^IIr^I/Ir^{II}Ir^{II}$ redox. Thus, the oxidation of **45a** was a more thermodynamically favorable process in comparison with that of the corresponding rhodium complex **46a** (−660 mV vs. Fc/Fc^+), which might explain the difference in the oxidative addition reactions between iridium **45a** and rhodium tetrametal complexes **46a**.

3.3 Raman Spectra of M–Mo–Mo–M (M = Pt, Pd, Ir, and Rh) Complexes. For discussion of the bonding nature of the linear skeleton comprised of M–Mo–Mo–M (M = Pt and Pd), single-crystal X-ray analysis is the best method to determine bonding distances. On the other hand, since we could not obtain crystals of all of them, Raman spectral data of ν(Mo–Mo) frequency served as a highly useful spectroscopic probe of elucidating the bonding nature. Figure 8 shows the plot of ν(Mo–Mo) frequency and the corresponding Mo–Mo distance determined by X-ray analyses. The frequency assigned to the quadruple Mo–Mo bond of M^{II} complexes and $[Mo_2(pyphos)_4]$ (**23**) were observed at 403–404 and 394 cm^{-1}, respectively, while the M^I complexes displayed a frequency assignable to ν(Mo–Mo) at 381–387 cm^{-1}, a lower wavenumber, being consistent with the longer Mo–Mo triple bond. The most attractive discussion concerns the Pd^0 and Pt^0 complexes, whose Raman spectral data are diverged in the range of 389–404 cm^{-1}, suggesting that the dative bond, $M^0 \rightarrow Mo^{II}$ was strong enough to elongate the Mo–Mo bond.

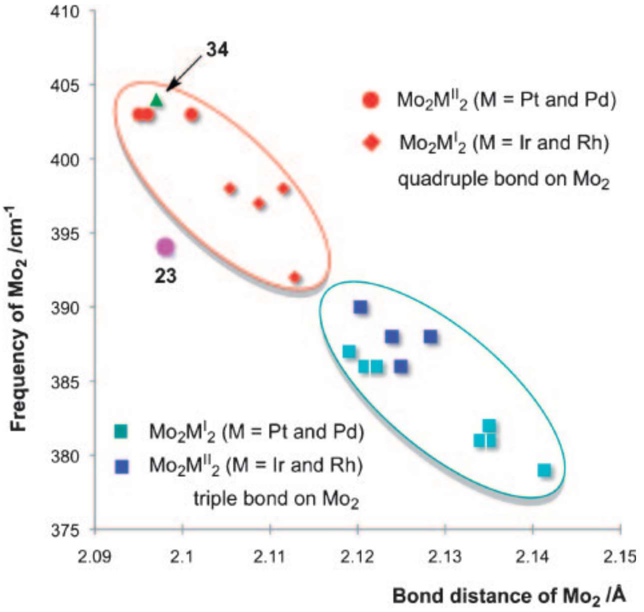


Figure 8. Plots of ν(Mo–Mo) (cm^{-1}) vs. bond distance of Mo–Mo (Å) for $[Mo_2(pyphos)_4]$ (**23**) and linear tetrametal complexes of M–Mo–Mo–M arrays (M = Pt, Pd, Ir, and Rh) including Pd^0 complex, $[Mo_2Pd_2(pyphos)_4]$ (**34**).

Among olefin-coordinated Pd^0 complexes $[Mo_2Pd_2(L)_2(pyphos)_4]$ (**35**) (**a**: L = acrylonitrile, **b**: L = fumaronitrile, and **c**: L = tetracyanoethylene), the wavenumber of ν(Mo–Mo) increased with an increase in the number of CN groups on the substrates, in the order of **35a** {389 cm^{-1}, comparable to that of the triply-bonded Mo_2 complexes, $[Mo_2Pd_2(pyphos)_4X_2]$ (**30a–30c**) (386–387 cm^{-1})} < **35b** (399 cm^{-1}) < **35c** {404 cm^{-1}, comparable to that of the quadruply-bonded Mo_2 complexes such as **23** (394 cm^{-1}) and Pd^{II} complexes, $[Mo_2Pd_2(pyphos)_4X_4]$ (**28a–28c**) (403 cm^{-1}), with no Mo–Pd bond}.[84] Thus, the increase in the number of electron-withdrawing substituents on the alkenes, acting as stronger π-acceptors, weakened the interaction between Pd^0 and Mo^{II}, as a consequence of the deformation of the palladium atoms from the axial vector of the Mo_2 core. Based on these argument, it is assumed that Pd^0 compounds **34** (389 cm^{-1}) and **35a** (389 cm^{-1})[84] and Pt^0 complexes (382–388 cm^{-1})[85] were in the range observed for M^I complexes, suggesting that the dative bond between M^0 and Mo^{II} is a rather strong bonding interaction. Compared with the group 10 metal series, plots for Ir^I and Rh^I complexes are close to those for Ir^{II} and Rh^{II} complexes, strongly suggesting that dative bonding interaction between M^I and Mo^{II} atoms are significantly contributed. One rational explanation for such interaction between M^I with Mo_2 core is ascribed to the contribution of dative bonding between M^I and Mo^{II}, the same as the bonding interaction between $M^0 \rightarrow Mo^{II}$ found for group 10 metals. Thus, the bonding nature of the tetrametal cluster systems could be evaluated based on data taken by Raman spectroscopy.

3.4 Cr_2M_2 (M = Pt and Pd) Complexes. Dichromium complex, $[Cr_2(pyphos)_4]$ (**49**) (Chart 11), analog to dimolybdenum complex **23**, was prepared in a similar manner applied to the synthesis of **23**.[97–99] The quadruply bonded Cr_2 moiety is known to be quite sensitive to the axially coordinating organic donor ligands,[100] however, there was no precedent example of axial coordination of metal ions. As a first trial, we started studying the influence of various d^8 Pt^{II} ions placed at axial positions of the Cr_2 moiety. Three Pt^{II} tetranuclear complexes, $[Cr_2Pt_2Cl_4(pyphos)_4]$ (**50**), $[Cr_2Pt_2Cl_2Me_2(pyphos)_4]$ (**51**), and

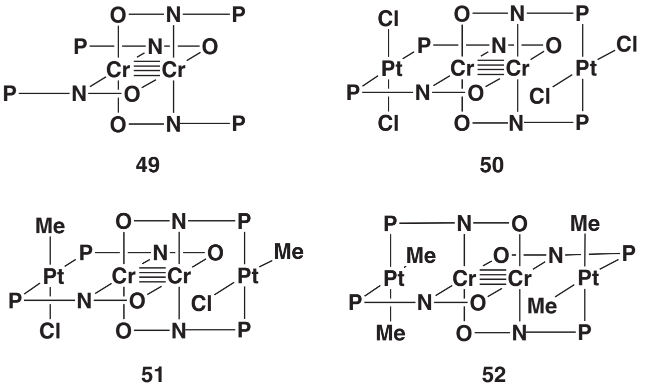


Chart 11.

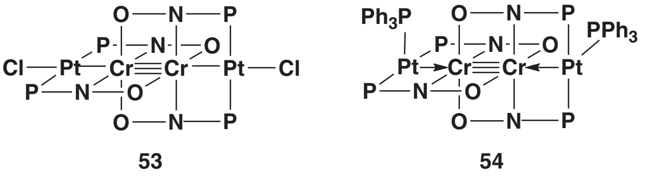


Chart 12.

[$Cr_2Pt_2Me_4$(pyphos)$_4$] (**52**) were prepared by the reaction of **49** with platinum(II) units such as $PtCl_2$, PtMeCl, and $PtMe_2$, respectively. Magnetic measurements of **50**–**52** along with the crystallographic study for the complex **52** revealed that the bond distances of the quadruply bonded Cr–Cr depended on the kind of substituents (Cl or Me) on the Pt atoms. Noteworthy was that $PtMe_2$ datively interacted with Cr_2 core to significantly elongate the Cr–Cr distance (2.389(9) Å). Such donating property of dialkyl- or diarylplatinum was already used for constructing heterometal clusters.[60]

We found that reduction of [$Cr_2Pt_2Cl_4$(pyphos)$_4$] (**50**) with $NaBHEt_3$ afforded [$Cr_2Pt_2Cl_2$(pyphos)$_4$] (**53**) (Chart 12), while a tetranuclear Pt^0 complex [$Cr_2Pt_2(PPh_3)_2$(pyphos)$_4$] (**54**) was prepared by the reaction of complex **49** with [$Pt(PPh_3)_4$] in THF, in consistent with the observed complexation of the molybdenum analogs. Complexes **53** and **54** were not isolated and accordingly characterized by only spectroscopic methods.

4. Conclusion

As briefly summarized in the introduction, over the last decades, several remarkable achievements in this attractive research field have been obtained and recently the research has been oriented toward molecular-based nanotechnology including molecular devices. We started this work in the early 90s. Polymerization of multiple bonded dinuclear metal complexes was considered as an ideal reaction for constructing such one-dimensional strings, however it was obviously quite difficult. As a consequence, our approaches have been directed to much shorter tetrametal systems, where we could find interesting chemistry for linearly aligned tetrametal complexes including multiple metal–metal bond in their skeletons. The addition of two metal units with unpaired orbitals to the quadruply-bonded Mo_2 core resulted in the formation of fully metal-to-metal bonded tetrametal fragments, M–Mo≡Mo–M, which are metalla-2-butyne. Most attractive feature of these complexes was the new triple bond at Mo–Mo moiety with a component of ($\pi^2\delta$). The author thus hopes that this account will become a hint for new ideas in this research field.

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References

1 *Multiple Bonds Between Metal Atoms*, 3rd ed., ed. by F. A. Cotton, C. A. Murio, R. A. Walton, Springer Science and Business Media, Oxford, **2005**.

2 J. Park, A. N. Pasupathy, J. I. Goldsmith, C. Chang, Y. Yaish, J. R. Petta, M. Rinkoski, J. P. Sethna, H. D. Abruña, P. L. McEuen, D. C. Ralph, *Nature* **2002**, *417*, 722.

3 W. Liang, M. P. Shores, M. Bockrath, J. R. Long, H. Park, *Nature* **2002**, *417*, 725.

4 D.-H. Chae, J. F. Berry, S. Jung, F. A. Cotton, C. A. Murillo, Z. Yao, *Nano Lett.* **2006**, *6*, 165.

5 I.-W. P. Chen, M.-D. Fu, W.-H. Tseng, J.-Y. Yu, S.-H. Wu, C.-J. Ku, C.-h. Chen, S.-M. Peng, *Angew. Chem., Int. Ed.* **2006**, *45*, 5814.

6 J.-D. Chen, F. A. Cotton, *J. Am. Chem. Soc.* **1991**, *113*, 5857.

7 F. A. Cotton, E. V. Dikarev, *J. Cluster Sci.* **1995**, *6*, 411.

8 R. N. McGinnis, T. R. Ryan, R. E. McCarley, *J. Am. Chem. Soc.* **1978**, *100*, 7900.

9 T. R. Ryan, R. E. McCarley, *Inorg. Chem.* **1982**, *21*, 2072.

10 F. A. Cotton, G. L. Powell, *Inorg. Chem.* **1983**, *22*, 871.

11 R. T. Carlin, R. E. McCarley, *Inorg. Chem.* **1989**, *28*, 3432.

12 F. A. Cotton, B. Hong, M. Shang, *Inorg. Chem.* **1993**, *32*, 4876.

13 M. H. Chisholm, D. L. Clark, K. Folting, J. C. Huffman, *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1014.

14 K. Krogmann, *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 35.

15 M.-N. Collomb-Dunand-Sauthier, A. Deronzier, R. Ziessel, *J. Chem. Soc., Chem. Commun.* **1994**, 189.

16 M.-N. Collomb-Dunand-Sauthier, A. Deronzier, R. Ziessel, *Inorg. Chem.* **1994**, *33*, 2961.

17 G. M. Finniss, E. Canadell, C. Campana, K. R. Dunbar, *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2772; M. E. Prater, L. E. Pence, R. Clérac, G. M. Finniss, C. Campana, P. Auban-Senzier, D. Jérome, E. Canadell, K. R. Dunbar, *J. Am. Chem. Soc.* **1999**, *121*, 8005.

18 S.-S. Chern, G.-H. Lee, S.-M. Peng, *J. Chem. Soc., Chem. Commun.* **1994**, 1645.

19 J. K. Barton, H. N. Rabinowitz, D. J. Szalda, S. J. Lippard, *J. Am. Chem. Soc.* **1977**, *99*, 2827; S. J. Lippard, *Science* **1982**, *218*, 1075; L. S. Hollis, S. J. Lippard, *J. Am. Chem. Soc.* **1983**, *105*, 3494; L. S. Hollis, S. J. Lippard, *Inorg. Chem.* **1983**, *22*, 2600; T. V. O'Halloran, M. M. Robert, S. J. Lippard, *Inorg. Chem.* **1986**, *25*, 957.

20 K. Matsumoto, K. Fuwa, *J. Am. Chem. Soc.* **1982**, *104*, 897; K. Matsumoto, H. Takahashi, K. Fuwa, *Inorg. Chem.* **1983**, *22*, 4086; K. Sakai, K. Matsumoto, *J. Am. Chem. Soc.* **1989**, *111*, 3074; K. Matsumoto, K. Sakai, K. Nishio, Y. Tokisue, R. Ito, T. Nishide, Y. Shichi, *J. Am. Chem. Soc.* **1992**, *114*, 8110; K. Sakai, M. Takeshita, Y. Tanaka, T. Ue, M. Yanagisawa, M. Kosaka, T.

Tsubomura, M. Ato, T. Nakano, *J. Am. Chem. Soc.* **1998**, *120*, 11353; K. Sakai, Y. Tanaka, Y. Tsuchiya, K. Hirata, T. Tsubomura, S. Iijima, A. Bhattacharjee, *J. Am. Chem. Soc.* **1998**, *120*, 8366; K. Sakai, E. Ishigami, Y. Konno, T. Kajiwara, T. Ito, *J. Am. Chem. Soc.* **2002**, *124*, 12088.

21 G. Trötscher, W. Micklitz, H. Schölhorn, U. Thewalt, B. Lippert, *Inorg. Chem.* **1990**, *29*, 2541.

22 A. L. Balch, M. M. Olmstead, *J. Am. Chem. Soc.* **1979**, *101*, 3128.

23 C. Tejel, M. A. Ciriano, J. A. López, F. J. Lahoz, L. A. Oro, *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1542; C. Tejel, M. A. Ciriano, L. A. Oro, *Chem.—Eur. J.* **1999**, *5*, 1131; C. Tejel, M. A. Ciriano, B. Eva Villarroya, R. Gelpi, J. A. López, F. J. Lahoz, L. A. Oro, *Angew. Chem., Int. Ed.* **2001**, *40*, 4084; C. Tejel, M. A. Ciriano, B. Eva Villarroya, J. A. López, F. J. Lahoz, L. A. Oro, *Angew. Chem., Int. Ed.* **2003**, *42*, 529.

24 A. L. Balch, J. R. Boehm, H. Hope, M. M. Olmstead, *J. Am. Chem. Soc.* **1976**, *98*, 7431.

25 R. H. Cayton, M. H. Chisholm, J. C. Huffman, E. B. Lobkovsky, *J. Am. Chem. Soc.* **1991**, *113*, 8709; D. V. Baxter, R. H. Cayton, M. H. Chisholm, J. C. Huffman, E. F. Putilina, S. L. Tagg, J. L. Wesemann, J. W. Zwanziger, F. D. Darrington, *J. Am. Chem. Soc.* **1994**, *116*, 4551; M. H. Chisholm, *Acc. Chem. Res.* **2000**, *33*, 53; M. H. Chisholm, N. J. Patmore, *Acc. Chem. Res.* **2007**, *40*, 19.

26 A. L. Balch, *Pure Appl. Chem.* **1988**, *60*, 555; A. L. Balch, *Prog. Inorg. Chem.* **1994**, *41*, 239.

27 S. Aduldecha, B. Hathaway, *J. Chem. Soc., Dalton Trans.* **1991**, 993; L.-P. Wu, P. Field, T. Morrissey, C. Murphy, P. Nagle, B. Hathaway, C. Simmons, P. Thornton, *J. Chem. Soc., Dalton Trans.* **1990**, 3835.

28 G. J. Pyrka, M. El-Mekki, A. A. Pinkerton, *J. Chem. Soc., Chem. Commun.* **1991**, 84.

29 M.-S. Tsai, S.-M. Peng, *J. Chem. Soc., Chem. Commun.* **1991**, 514; E.-C. Yang, M.-C. Cheng, M.-S. Tsai, S.-M. Peng, *J. Chem. Soc., Chem. Commun.* **1994**, 2377; J.-T. Sheu, C.-C. Lin, I. Chao, C.-C. Wang, S.-M. Peng, *Chem. Commun.* **1996**, 315; W.-H. Chan, S.-M. Peng, C.-M. Che, *J. Chem. Soc., Dalton Trans.* **1998**, 2867; H. Li, G.-H. Lee, S.-M. Peng, *Inorg. Chem. Commun.* **2003**, *6*, 1; T.-B. Tsao, G.-H. Lee, C.-Y. Yeh, S.-M. Peng, *Dalton Trans.* **2003**, 1465; H. Li, G.-H. Lee, S.-M. Peng, *J. Mol. Struct.* **2004**, *707*, 179; M.-Y. Huang, C.-Y. Yeh, G.-H. Lee, S.-M. Peng, *Dalton Trans.* **2006**, 5683; R. H. Ismayilov, W.-Z. Wang, G.-H. Lee, R.-R. Wang, I. P.-C. Liu, C.-Y. Yeh, S.-M. Peng, *Dalton Trans.* **2007**, 2898; C.-K. Kuo, I. P.-C. Liu, C.-Y. Yeh, C.-H. Chou, T.-B. Tsao, G.-H. Lee, S.-M. Peng, *Chem.—Eur. J.* **2007**, *13*, 1442.

30 M.-M. Rohmer, M. Bénard, *J. Am. Chem. Soc.* **1998**, *120*, 9372.

31 F. A. Cotton, L. M. Daniels, C. A. Murillo, I. Pascual, *J. Am. Chem. Soc.* **1997**, *119*, 10223; F. A. Cotton, L. M. Daniels, G. T. Jordan, IV, C. A. Murillo, *J. Am. Chem. Soc.* **1997**, *119*, 10377; F. A. Cotton, L. M. Daniels, C. A. Murillo, *Chem. Commun.* **1998**, 39; F. A. Cotton, L. M. Daniels, C. A. Murillo, X. Wang, C. A. Murillo, *Chem. Commun.* **1999**, 2461; R. Clérac, F. A. Cotton, K. R. Dunbar, C. A. Murillo, I. Pascual, X. Wang, *Inorg. Chem.* **1999**, *38*, 2655; R. Clérac, F. A. Cotton, L. M. Daniels, K. R. Dunbar, C. A. Murillo, X. Wang, *Inorg. Chem.* **2001**, *40*, 1256; R. Clérac, F. A. Cotton, L. M. Daniels, K. R. Dunbar, C. A. Murillo, H.-C. Zhou, *Inorg. Chem.* **2000**, *39*, 3414; R. Clérac, F. A. Cotton, L. M. Daniels, K. R. Dunbar, C. A. Murillo, I. Pascual, *Inorg. Chem.* **2000**, *39*, 748; R. Clérac, F. A. Cotton, L. M. Daniels, K. R. Dunbar, K. Kirschbaum, C. A. Murillo, A. A. Pinkerton, A. J. Schultz, X. Wang, *J. Am. Chem. Soc.* **2000**, *122*, 6226; R. Clérac, F. A. Cotton, K. R. Dunbar, T. Lu, C. A. Murillo, X. Wang, *Inorg. Chem.* **2000**, *39*, 3065; R. Clérac, F. A. Cotton, S. P. Jeffery, C. A. Murillo, X. Wang, *Inorg. Chem.* **2001**, *40*, 1265; R. Clérac, F. A. Cotton, L. M. Daniels, K. R. Dunbar, C. A. Murillo, I. Pascual, *Inorg. Chem.* **2000**, *39*, 752; R. Clérac, F. A. Cotton, K. R. Dunbar, T. Lu, C. A. Murillo, X. Wang, *J. Am. Chem. Soc.* **2000**, *122*, 2272; J. F. Berry, F. A. Cotton, L. M. Daniels, C. A. Murillo, *J. Am. Chem. Soc.* **2002**, *124*, 3212; J. F. Berry, F. A. Cotton, P. Lei, C. A. Murillo, *Inorg. Chem.* **2003**, *42*, 377; F. A. Cotton, P. Lei, C. A. Murillo, *Inorg. Chim. Acta* **2003**, *349*, 173; F. A. Cotton, P. Lei, C. A. Murillo, *Inorg. Chim. Acta* **2003**, *351*, 183; J. F. Berry, F. A. Cotton, L. M. Daniels, C. A. Murillo, X. Wang, *Inorg. Chem.* **2003**, *42*, 2418; J. F. Berry, F. A. Cotton, T. Lu, C. A. Murillo, B. K. Roberts, X. Wang, *J. Am. Chem. Soc.* **2004**, *126*, 7082; M. Bénard, J. F. Berry, F. A. Cotton, C. Gaudin, X. López, C. A. Murillo, M.-M. Rohmer, *Inorg. Chem.* **2006**, *45*, 3932; J. F. Berry, F. A. Cotton, C. A. Murillo, *Inorg. Chim. Acta* **2004**, *357*, 3847.

32 F. A. Cotton, L. M. Daniels, P. Lei, C. A. Murillo, X. Wang, *Inorg. Chem.* **2001**, *40*, 2778.

33 X. López, M.-Y. Huang, G.-C. Huang, S.-M. Peng, F.-Y. Li, M. Bénard, M.-M. Rohmer, *Inorg. Chem.* **2006**, *45*, 9075.

34 S.-J. Shieh, C.-C. Chou, G.-H. Lee, C.-C. Wang, S.-M. Peng, *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 56.

35 C.-C. Wang, W.-C. Lo, C.-C. Chou, G.-H. Lee, J.-M. Chen, S.-M. Peng, *Inorg. Chem.* **1998**, *37*, 4059.

36 H.-C. Chang, J.-T. Li, C.-C. Wang, T.-W. Lin, H.-C. Lee, G.-H. Lee, G.-H. Lee, S.-M. Peng, *Eur. J. Inorg. Chem.* **1999**, 1243.

37 C.-Y. Yeh, C.-H. Chou, K.-C. Pan, C.-C. Wang, G.-H. Lee, Y. O. Su, S.-M. Peng, *J. Chem. Soc., Dalton Trans.* **2002**, 2670.

38 C.-Y. Yeh, Y.-L. Chiang, G.-H. Lee, S.-M. Peng, *Inorg. Chem.* **2002**, *41*, 4096.

39 W.-Z. Wang, R. H. Ismayilov, G.-H. Lee, I. P.-C. Liu, C.-Y. Yeh, S.-M. Peng, *Dalton Trans.* **2007**, 830.

40 C. Yin, G.-C. Huang, C.-K. Kuo, M.-D. Fu, H.-C. Lu, J.-H. Ke, K.-N. Shih, Y.-L. Huang, G.-H. Lee, C.-Y. Yeh, C.-H. Chen, S.-M. Peng, *J. Am. Chem. Soc.* **2008**, *130*, 10090.

41 J. F. Berry, F. A. Cotton, P. Lei, T. Lu, C. A. Murillo, *Inorg. Chem.* **2003**, *42*, 3534.

42 I. P.-C. Liu, M. Bénard, H. Hasanov, I.-W. P. Chen, W.-H. Tseng, M.-D. Fu, M.-M. Rohmer, C.-h. Chen, G.-H. Lee, S.-M. Peng, *Chem.—Eur. J.* **2007**, *13*, 8667.

43 T.-B. Tsao, S.-S. Lo, C.-Y. Yeh, G.-H. Lee, S.-M. Peng, *Polyhedron* **2007**, *26*, 3833.

44 C.-H. Chien, J.-C. Chang, C.-Y. Yeh, G.-H. Lee, J.-M. Fang, S.-M. Peng, *Dalton Trans.* **2006**, 2106.

45 Y.-H. Chen, C.-C. Lee, C.-C. Wang, G.-H. Lee, S.-Y. Lai, F.-Y. Li, C.-Y. Mou, S.-M. Peng, *Chem. Commun.* **1999**, 1667.

46 S.-Y. Lai, T.-W. Lin, Y.-H. Chen, C.-C. Wang, G.-H. Lee, M.-H. Yang, M.-K. Leung, S.-M. Peng, *J. Am. Chem. Soc.* **1999**, *121*, 250.

47 H. Hasan, U.-K. Tan, G.-H. Lee, S.-M. Peng, *Inorg. Chem. Commn.* **2007**, *10*, 983.

48 R. H. Ismayilov, W.-Z. Wang, R.-R. Wang, C.-Y. Yeh, G.-H. Lee, S.-M. Peng, *Chem. Commun.* **2007**, 1121.

49 S.-M. Peng, C.-C. Wang, Y.-L. Jang, Y.-H. Chen, F.-Y. Li, C.-Y. Mou, M.-K. Leung, *J. Magn. Magn. Mater.* **2000**, *209*, 80.

50 Y. Yamamoto, T. Tanase, H. Ukaji, M. Hasegawa, T. Igoshi, K. Yoshimura, *J. Organomet. Chem.* **1995**, *498*, C23; T. Tanase, E. Goto, R. A. Begum, M. Hamaguchi, S. Zhan, M. Iida, K. Sakai,

Organometallics **2004**, *23*, 5975.

51 E. Goto, R. A. Begum, S. Zhan, T. Tanase, K. Tanigaki, K. Sakai, *Angew. Chem., Int. Ed.* **2004**, *43*, 5029.

52 A. L. Balch, E. Y. Fung, M. M. Olmstead, *J. Am. Chem. Soc.* **1990**, *112*, 5181.

53 V. M. Miskowski, I. S. Sigal, K. R. Mann, H. B. Gray, S. J. Milder, G. S. Hammond, P. R. Ryason, *J. Am. Chem. Soc.* **1979**, *101*, 4383.

54 I. S. Sigal, K. R. Mann, H. B. Gray, *J. Am. Chem. Soc.* **1980**, *102*, 7252.

55 K. R. Mann, M. J. DiPierro, T. P. Gill, *J. Am. Chem. Soc.* **1980**, *102*, 3965.

56 T. Zhang, M. Drouin, P. D. Harvey, *Inorg. Chem.* **1999**, *38*, 1305; T. Zhang, M. Drouin, P. D. Harvey, *Inorg. Chem.* **1999**, *38*, 957.

57 T. Murahashi, E. Mochizuki, Y. Kai, H. Kurosawa, *J. Am. Chem. Soc.* **1999**, *121*, 10660; T. Murahashi, Y. Higuchi, T. Katoh, H. Kurosawa, *J. Am. Chem. Soc.* **2002**, *124*, 14288; T. Murahashi, H. Nakashima, T. Nagai, Y. Mino, T. Okuno, M. Abdul Jalil, H. Kurosawa, *J. Am. Chem. Soc.* **2006**, *128*, 4377; T. Murahashi, T. Uemura, H. Kurosawa, *J. Am. Chem. Soc.* **2003**, *125*, 8436; T. Murahashi, S. Ogoshi, H. Kurosawa, *Chem. Rec.* **2003**, *3*, 101; Y. Tatsumi, T. Naga, H. Nakashima, T. Murahashi, H. Kurosawa, *Chem. Commun.* **2004**, 1430; Y. Tatsumi, T. Murahashi, M. Okada, S. Ogoshi, H. Kurosawa, *Chem. Commun.* **2008**, 477; T. Murahashi, M. Fujimoto, Y. Kawabata, R. Inoue, S. Ogoshi, H. Kurosawa, *Angew. Chem., Int. Ed.* **2007**, *46*, 5440; T. Murahashi, M. Fujimoto, M. Oka, Y. Hashimoto, T. Uemura, Y. Tatsumi, Y. Nakao, A. Ikeda, S. Sakaki, H. Kurosawa, *Science* **2006**, *313*, 1104; T. Murahashi, N. Kato, T. Uemura, H. Kurosawa, *Angew. Chem., Int. Ed.* **2007**, *46*, 3509; T. Murahashi, Y. Hashimoto, K. Chiyoda, M. Fujimoto, T. Uemura, R. Inoue, S. Ogoshi, H. Kurosawa, *J. Am. Chem. Soc.* **2008**, *130*, 8586; T. Murahashi, R. Inoue, K. Usui, S. Ogoshi, *J. Am. Chem. Soc.* **2009**, *131*, 9888.

58 P. Pyykkö, *Chem. Rev.* **1997**, *97*, 597.

59 R. Usón, A. Laguna, M. Laguna, J. Jiménez, P. G. Jones, *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 198; A. Laguna, M. Laguna, J. Jimenez, F. J. Lahoz, E. Olmos, *Organometallics* **1994**, *13*, 253.

60 T. Yamaguchi, F. Yamazaki, T. Ito, *J. Am. Chem. Soc.* **2001**, *123*, 743.

61 A. Schreiber, O. Krizanovic, E. C. Fusch, B. Lippert, F. Lianza, A. Albinati, S. Hill, D. M. L. Goodgame, H. Stratemeier, M. A. Hitchman, *Inorg. Chem.* **1994**, *33*, 6101.

62 D. M. L. Goodgame, R. W. Rollins, B. Lippert, *Polyhedron* **1985**, *4*, 829; D. Neugebauer, B. Lippert, *J. Am. Chem. Soc.* **1982**, *104*, 6596; B. Lippert, U. Thewalt, H. Schöllhorn, D. M. L. Goodgame, R. W. Rollins, *Inorg. Chem.* **1984**, *23*, 2807; B. Lippert, W. Micklitz, O. Renn, G. Trötscher, I. Dieter, G. Frommer, *Pure Appl. Chem.* **1990**, *62*, 1075.

63 H. H. Murray, D. A. Briggs, G. Garzón, R. G. Raptis, L. C. Porter, J. P. Fackler, Jr., *Organometallics* **1987**, *6*, 1992.

64 S. Wang, G. Garzón, C. King, J.-C. Wang, J. P. Fackler, Jr., *Inorg. Chem.* **1989**, *28*, 4623.

65 A. L. Balch, J. K. Nagle, M. M. Olmstead, P. E. Reedy, Jr., *J. Am. Chem. Soc.* **1987**, *109*, 4123; A. L. Balch, J. K. Nagle, D. E. Oram, P. E. Reedy, *J. Am. Chem. Soc.* **1988**, *110*, 454; A. L. Balch, M. M. Olmstead, D. E. Oram, P. E. Reedy, Jr., S. H. Reimer, *J. Am. Chem. Soc.* **1989**, *111*, 4021; A. L. Balch, V. J. Catalano, M. M. Olmstead, *J. Am. Chem. Soc.* **1990**, *112*, 2010; A. L. Balch, V. J. Catalano, B. C. Noll, M. M. Olmstead, *J. Am. Chem. Soc.* **1990**, *112*, 7558; A. L. Balch, B. J. Davis, M. M. Olmstead, *Inorg. Chem.* **1990**, *29*, 3066; A. L. Balch, V. J. Catalano, M. A. Chatfield, J. K. Nagle, M. M. Olmstead, P. E. Reedy, Jr., *J. Am. Chem. Soc.* **1991**, *113*, 1252.

66 R. Clérac, F. A. Cotton, K. R. Dunbar, C. A. Murillo, X. Wang, *Inorg. Chem.* **2001**, *40*, 420.

67 F. A. Cotton, B. E. Hanson, *Inorg. Chem.* **1978**, *17*, 3237.

68 F. A. Cotton, P. E. Fanwick, R. H. Niswander, J. C. Sekutowski, *J. Am. Chem. Soc.* **1978**, *100*, 4725.

69 W. Clegg, C. D. Garner, L. Akhter, M. H. Al-Samman, *Inorg. Chem.* **1983**, *22*, 2466.

70 A. L. Balch, *Prog. Inorg. Chem.* **1994**, *41*, 239.

71 M. Tanaka, Ph.D. Thesis, Osaka University, Osaka, **1998**.

72 K. Mashima, M. Tanaka, K. Tani, H. Nakano, A. Nakamura, *Inorg. Chem.* **1996**, *35*, 5244.

73 K. Mashima, Y. Kaneda, A. Fukumoto, M. Tanaka, K. Tani, H. Nakano, A. Nakamura, *Inorg. Chim. Acta* **1998**, *270*, 459.

74 K. Mashima, H. Nakano, A. Nakamura, *J. Am. Chem. Soc.* **1993**, *115*, 11632.

75 K. Mashima, H. Nakano, A. Nakamura, *J. Am. Chem. Soc.* **1996**, *118*, 9083.

76 K. Mashima, M. Tanaka, Y. Kaneda, A. Fukumoto, H. Mizomoto, K. Tani, H. Nakano, A. Nakamura, T. Sakaguchi, K. Kamada, K. Ohta, *Chem. Lett.* **1997**, 411.

77 K. Kamada, K. Ohta, Y. Shimoyama, T. Miyabayashi, K. Mashima, *Opt. Mater.* **2004**, *27*, 573.

78 H. Nakano, A. Nakamura, K. Mashima, *Inorg. Chem.* **1996**, *35*, 4007.

79 H. Nakano, Ph.D. Thesis, Osaka University, Osaka, **1996**.

80 G.-L. Xu, M. C. DeRosa, R. J. Crutchley, T. Ren, *J. Am. Chem. Soc.* **2004**, *126*, 3728.

81 J. F. Berry, F. A. Cotton, C. A. Murillo, *Organometallics* **2004**, *23*, 2503.

82 C.-K. Kuo, J.-C. Chang, C.-Y. Yeh, G.-H. Lee, C.-C. Wang, S.-M. Peng, *Dalton Trans.* **2005**, 3696.

83 K. Mashima, A. Fukumoto, H. Nakano, Y. Kaneda, K. Tani, A. Nakamura, *J. Am. Chem. Soc.* **1998**, *120*, 12151.

84 K. Mashima, A. Shima, K. Nakao, A. Fukumoto, Y. Kaneda, Y. Kusumi, *Inorg. Chem.* **2009**, *48*, 1879.

85 K. Mashima, Y. Shimoyama, Y. Kusumi, A. Fukumoto, T. Yamagata, M. Ohashi, *Eur. J. Inorg. Chem.* **2007**, 235.

86 A. L. Balch, C. T. Hunt, C.-L. Lee, M. M. Olmstead, J. P. Farr, *J. Am. Chem. Soc.* **1981**, *103*, 3764.

87 T. Kawamura, H. Katayama, H. Nishikawa, T. Yamabe, *J. Am. Chem. Soc.* **1989**, *111*, 8156; T. Kawamura, M. Maeda, M. Miyamoto, H. Usami, K. Imaeda, M. Ebihara, *J. Am. Chem. Soc.* **1998**, *120*, 8136.

88 E. W. Stern, P. K. Maples, *J. Catal.* **1972**, *27*, 134; E. W. Stern, P. K. Maples, *J. Catal.* **1972**, *27*, 120.

89 R. U. Kirss, R. Eisenberg, *Inorg. Chem.* **1989**, *28*, 3372.

90 T. Tsubomura, K. Sakai, *Coord. Chem. Rev.* **1998**, *171*, 107.

91 M. S. Balakrishna, S. S. Krishnamurthy, R. Murugavel, M. Nethaji, I. I. Mathews, *J. Chem. Soc., Dalton Trans.* **1993**, 477.

92 R. A. Klein, P. Witte, R. van Belzen, J. Fraanje, K. Goubitz, M. Numan, H. Schenk, J. M. Ernsting, C. J. Elsevier, *Eur. J. Inorg. Chem.* **1998**, 319.

93 Y. Pan, J. T. Mague, M. J. Fink, *J. Am. Chem. Soc.* **1993**, *115*, 3842.

94 A. Döhring, R. Goddard, G. Hopp, P. W. Jolly, N. Kokel, C. Krüger, *Inorg. Chim. Acta* **1994**, *222*, 179.

95 T. Rüffer, M. Ohashi, A. Shima, H. Mizomoto, Y. Kaneda, K. Mashima, *J. Am. Chem. Soc.* **2004**, *126*, 12244.

96 M. Ohashi, A. Shima, T. Rüffer, H. Mizomoto, Y. Kaneda,

K. Mashima, *Inorg. Chem.* **2007**, *46*, 6702.
97 K. Mashima, M. Tanaka, K. Tani, A. Nakamura, S. Takeda, W. Mori, K. Yamaguchi, *J. Am. Chem. Soc.* **1997**, *119*, 4307.
98 M. Tanaka, K. Mashima, M. Nishino, S. Takeda, W. Mori, K. Tani, K. Yamaguchi, A. Nakamura, *Bull. Chem. Soc. Jpn.* **2001**, *74*, 67.
99 Y. Kitagawa, S. Nakano, T. Kawakami, K. Mashima, K. Yamaguchi, *Polyhedron* **2003**, *22*, 2019.
100 F. A. Cotton, H. Chen, L. M. Daniels, X. Feng, *J. Am. Chem. Soc.* **1992**, *114*, 8980.

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