

Oxidative Reactions of Tetrametal Pd(0)···Mo(II)—Mo(II)···Pd(0) Clusters: Electrochemical Communication of Two Pd(0) Centers through the Mo₂ Moiety and Oxidative Formation of a Pd(I)—Mo(II)—Mo(II)—Pd(I) Array

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Received July 26, 2008

Reaction of Mo₂(pyphos)₄ (**1**) (pyphos = 6-diphenylphosphino-2-pyridonate) with Pd(dba)₂ (dba = dibenzylideneacetone) afforded the Pd(0) complex Mo₂Pd₂(pyphos)₄ (**2**) which has two Pd(0) centers at both axial positions of the Mo₂ core. The unsaturated Pd(0) centers of **2** were coordinated with donor molecules such as olefins, acetylenes, isonitriles, carbon monoxide, and triphenylphosphine to give the corresponding adducts, Mo₂Pd₂(pyphos)₄(L)₂ (**3a**: L = acrylonitrile, **3b**: L = fumaronitrile, **3c**: L = tetracyanoethylene, **3d**: L = diisopropyl fumarate, **3e**: L = diethyl fumarate, **3f**: L = dimethyl fumarate, **3g**: L = dimethyl maleate, **3h**: L = 2,6-xylylisocyanide, **3i**: L = *tert*-butylisocyanide, **3j**: L = dimethyl acetylenedicarboxylate, **3k**: L = 1,4-benzoquinone, **3l**: L = 1,4-naphthoquinone, **3m**: L = carbon monoxide, and **3n**: L = triphenylphosphine). Oxidative 1,4-addition of ArSSAr and benzoyl peroxide to the Pd(0) centers of **2** afforded the corresponding Pd(I) complexes Mo₂Pd₂(SAr)₂(pyphos)₄ (**7a**: Ar = C₆H₅, **7b**: Ar = 4-Me₃CC₆H₄, **7c**: Ar = 4-MeC₆H₄, **7d**: 4-NO₂C₆H₄) and Mo₂Pd₂(OCOPh)₂(pyphos)₄ (**9**). Chemical oxidation of **2** with [Cp₂Fe][BF₄]₂ in CH₃CN afforded a dicationic Pd(I) complex [Mo₂Pd₂(pyphos)₄(CH₃CN)₂][BF₄]₂ (**10a**). Similarly, the reaction of **2** with [Cp₂Fe][BF₄]₂ in the presence of excess amounts of various donor molecules in THF gave rise to corresponding dicationic Pd(I) complexes [Mo₂Pd₂(pyphos)₄(L')₂][BF₄]₂ (**10b**; L' = dimethylsulfoxide, **10c**: L' = THF, **10d**: L' = benzonitrile, **10e**: L' = *p*-methoxyphenylnitrile, **10f**: L' = *p*-trifluoromethylphenylnitrile, **10g**: L' = pyridine, and **10h**: L' = *p*-dimethylaminopyridine), whereas complexes [Mo₂Pd₂(pyphos)₄(CNXyl)₂][BF₄]₂ (**10i**) and [Mo₂Pd₂(pyphos)₄(CN^tBu)₂][BF₄]₂ (**10j**) were prepared by oxidation of the corresponding isonitrile-Pd(0) complexes **3h** and **3i**. Cyclic voltammetry of **10a–j** displayed two different oxidation profiles of Pd(0) depending on the donor molecules: complexes **10a–f** showed two waves ascribed to electron communication through monocationic species as intermediates, whereas complexes **10g–j** showed one wave due to two-electron process. Furthermore, the oxidative addition of alkyl and aryl halides to **2** gave rise to two different reaction patterns: excess amounts of benzyl halides BnX (X = Cl, Br, I), PhCl, and PhBr, and 2 equiv of PhI reacted with **2** to give Pd(I) complexes Mo₂Pd₂(X)₂(pyphos)₄ (**4a**: X = Cl, **4b**: X = Br, **4c**: X = I), and the reactions of **2** with excess amounts of PhI and MeI afforded Pd(II) complexes Mo₂Pd₂(Ph)₂(pyphos)₄ (**11**) and Mo₂Pd₂(CH₃)₂(pyphos)₄ (**13**) bearing two “Pd(Ph)” and “Pd(CH₃)” moieties.

Introduction

Multinuclear transition metal complexes are currently attracting increased attention because of their intrinsic bonding nature including metal–metal bonds, dimensionally

controlled assembly of metals leading to nanomaterials, and diverse reactivity reflecting redox reactions through any mixed valence species.^{1–6} Even dinuclear complexes exhibit a different coordination chemistry, as well as different

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cooperative organic transformation from those of mononuclear complexes. Particular examples are d^{10} closed shell dinuclear palladium complexes, $\text{Pd}_2(\mu\text{-dppm})_3$ [DPPM = bis(diphenylphosphino)methane],^{7–9} $\text{Pd}_2(\mu\text{-dmpm})_3$ [DMPM = bis(dimethylphosphino)methane],¹⁰ $\text{Pd}_2[\mu\text{-MeN}(\text{P}(\text{OPh})_2)_2]_3$,¹¹ $\text{Pd}_2(\mu\text{-dafo})(1,4\text{-benzoquinone})_2$ (DAFO = 4,5-diazafluorene-9-one),¹² and $\text{Pd}_2[\mu\text{-CH}_2(\text{PR}_2)]_2$ [R = *i*Pr and *c*-C₆H₁₁],^{13,14} which have unique attractive bonding interaction between two Pd(0) atoms through d-p mixed σ -bonding orbitals.¹⁵ Such bonding interactions not only compensate for the unsaturation around the Pd(0) centers but also exhibit a long-duration emitting-state and cooperative organic transformations.^{8,16–20} In addition, unique bonding interactions among multimetal Pd(0) clusters supported by conjugated polyene ligands were recently reported.²¹ In contrast to these homopolymetal Pd(0) complexes, there are relatively few examples of heterometallic clusters containing dative Pd(0)–M interactions,^{22–24} though it was recently reported that some d^{10} metals such as Au(I), Ag(I), and Pt(0) have noncovalent, attractive bonding interactions with other metals that have a closed-shell d^{10} electronic configuration and with heavier metals that have a closed-shell s^2 electronic configuration.^{25–38}

We studied linear heterometallic cluster complexes supported by a bridging tridentate ligand, 6-diphenylphosphino-2-pyridonate (= pyphos), in which three different elements, P, N, and O, linearly aligned by a rigid pyridone framework can support two different transition metal types.^{39–47} On the basis of this strategy, we reported a reaction of $\text{Mo}_2(\text{pyphos})_4$

(**1**) with a Pd(0) complex to give a tetranuclear complex, $\text{Mo}_2\text{Pd}_2(\text{pyphos})_4$ (**2**), which contains zero-valent palladium atoms at both axial positions of a quadruply bonded Mo₂ core.⁴⁴ Here, we report the reaction of **2** with various π -ligands such as phosphine, olefins, alkyne, isocyanides, and carbon monoxide and oxidative reactions of **2** toward oxidants such as disulfides, benzoyl peroxide, and alkyl and phenyl halides through a stepwise oxidation process to form the corresponding Pd(I) species, which are markedly different from the mononuclear Pd(0) complexes, and oxidative addition of excess amounts of PhI and CH₃I to **2** afforded the corresponding Pd(II) species.

Results and Discussion

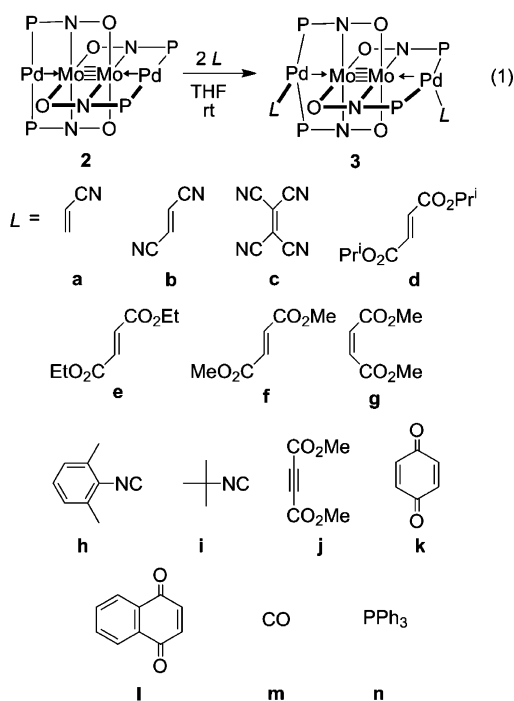
Reaction of Complex 2 with Donor Molecules. Because the two Pd(0) in **2** are highly unsaturated, donor molecules such as olefins, acetylenes, isonitriles, carbon monoxide, and triphenylphosphine are coordinated to the Pd(0) center. The addition of donor molecules to **2** in THF immediately gave rise to the corresponding adducts, $\text{Mo}_2\text{Pd}_2(\text{pyphos})_4(L)_2$ (**3a**: $L = \text{acrylonitrile}$,⁴⁴ **3b**: $L = \text{fumaronitrile}$,⁴⁴ **3c**: $L = \text{tetracyanoethylene}$,⁴⁴ **3d**: $L = \text{diisopropyl fumarate}$, **3e**: $L = \text{diethyl fumarate}$, **3f**: $L = \text{dimethyl fumarate}$, **3g**: $L = \text{dimethyl maleate}$, **3h**: $L = 2,6\text{-xylylisocyanide}$, **3i**: $L = \text{tert-butylisocyanide}$, **3j**: $L = \text{dimethyl acetylenedicarboxylate}$, **3k**: $L = 1,4\text{-benzoquinone}$, **3l**: $L = 1,4\text{-naphthoquinone}$, **3m**: $L = \text{carbon monoxide}$, **3n**: $L = \text{triphenylphosphine}$) (eq 1), and their selected spectral data are summarized in Table 1.

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Table 1. Selected Spectral Data for **3**

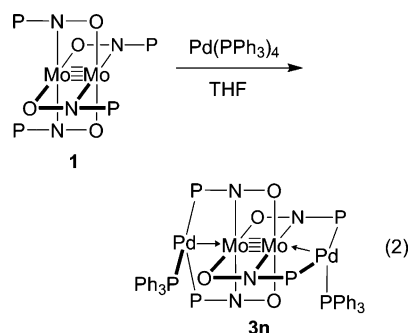
	³¹ P{ ¹ H} NMR	IR	Raman
	δ/[ppm] ^a		
3a^d	26.0 (s)	2201	389
3b^d	26.2 (s)	2213	399
3b'	25.2 (s)	2200	
3c^d	20.8 (s)	2224	404
3d	23.5 (s)	1699	388
3e	24.4 (s)	1701	392
3e'		1696, 1712	
3g	26.3 (s)	1702	
3h	25.7 (s)	2060 ^f	388
3i	25.4 (s)	2105 ^f	389
3j	31.6 (s)	1691, 1851 ^g	395
3k^h	26.8 (s)		
3l^h	25.7 (s)		
3m^h	25.8 (s)	1997 ⁱ	
3n	26.7, 27.6 ^j		389

^a Measured in C₆D₆ at 35 °C. ^b Measured in nujol mull, ν(C=O). ^c ν(Mo—Mo) by 457.9 nm laser excitation. ^d Ref 44. ^e Decomposed upon dissolving in typical organic solvent. ^f ν(C≡N). ^g ν(C≡C). ^h Not isolated. ⁱ Measured in C₆H₆ solution under CO atmosphere, ν(C≡O). ^j A signal due to PPh₃ at δ 20.3.



The ¹H NMR spectral data of these complexes except for **3f**, which does not dissolve in organic solvents without decomposing, clearly revealed a 2:1 ratio of pyphos ligands and donors, consistent with the formulation of **3**. IR spectra of olefin complexes **3a–g** displayed a C=O or C≡N stretching frequency lower by 20–55 cm⁻¹ than that of the corresponding free olefins, and the C=C stretching frequency of complex **3j** was observed at 1851 cm⁻¹. The ³¹P{¹H} NMR spectra of all these complexes showed a singlet resonance in the range of δ 20.8–31.6 assignable to the phosphorus nuclei bound to the Pd(0) center. The reactions of **2** with 1,4-benzoquinone and 1,4-naphthoquinone immediately produced the corresponding adducts **3k** and **3l** whose ³¹P{¹H} NMR spectra displayed a singlet at δ 26.8 and 25.7, respectively, due to the corresponding olefin

adducts. These products, however, gradually decomposed. When **2** was exposed to CO (1 atm), the color of the solution of Mo₂Pd₂(pyphos)₄(CO)₂ (**3m**), whose IR spectrum showed a sharp absorption at 1997 cm⁻¹ due to CO bound to the palladium center, which immediately turned to bright orange. Under reduced pressure, CO of **3m** was quickly released and then **3m** turned back to **2**. Treatment of **2** with PPh₃ resulted in the formation of Mo₂Pd₂(pyphos)₄(PPh₃)₂ (**3n**), which was alternatively obtained by the reaction of **1** with 2 equiv of Pd(PPh₃)₄ (eq 2).



Each Pd(0) center in **3n** was determined to have a trigonal planar geometry based on its ³¹P{¹H} NMR spectrum that displayed an ABX pattern due to the two phosphorus atoms of the two pyphos ligands and a phosphorus atom of PPh₃. The ³¹P{¹H} NMR spectrum of **3n** at -40 °C and its simulated spectrum showed three doublets of doublets centered at δ 27.6, 26.7, and 20.3 and three coupling *J*_{P-P} constants at 80, 84, and 100 Hz (Figure 1), whose chemical shift values and coupling constants were almost the same as those for the corresponding Mo₂Pt₂(pyphos)₄(PR₃)₂ complexes,⁴⁷ indicating that the Pd center is surrounded by three phosphorus atoms in a distorted trigonal planar geometry. A comparable coupling constant (*J*_{P-P} = 110 Hz) was also reported for a dinuclear trigonal planar platinum complex, Pt₂(μ-dppm)₃.⁴⁸

In the ¹H NMR spectrum of **3n**, protons due to pyphos ligands were assigned with the ¹H–¹H COSY together with ¹H{³¹P} NMR spectrum at -40 °C. The ¹H NMR spectrum of **3n** showed a temperature dependency in solution, likely because of the rapid process of dissociation and re-coordination of PPh₃ through the intermediate species **2**. The activation parameters for **3n** were estimated to be Δ*G*[‡] (298) = 13(1) kcal/mol, Δ*H*[‡] = 11.3(6) kcal/mol, and Δ*S*[‡] = -6(2) eu based on iterative simulation of its ¹H NMR spectra in the temperature range of 60 to -60 °C. This process involving the dissociation and the re-coordination of PPh₃ was further supported by the ³¹P{¹H} NMR measurement: below 20 °C the addition of 1 equiv of PPh₃ to **3n** resulted in broadening of two signals due to the coordinated PPh₃ (δ 20.3) and free PPh₃ (δ -4.3), and above 20 °C these two peaks started to coalesce. These observations were consistent to the substitution reaction of a Pt analogue, Mo₂Pt₂(pyphos)₄(PPh₃)₂, with excess amounts of some phosphine and phosphite ligands, affording to the corresponding adducts.⁴⁷

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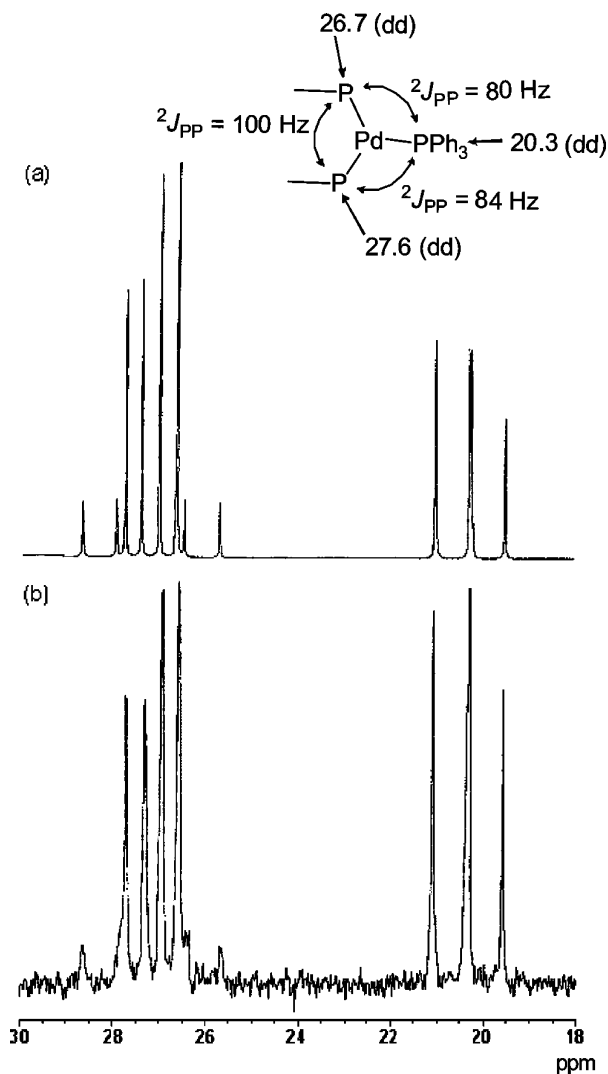
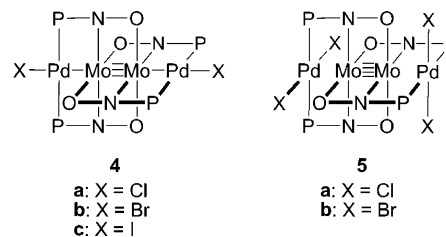


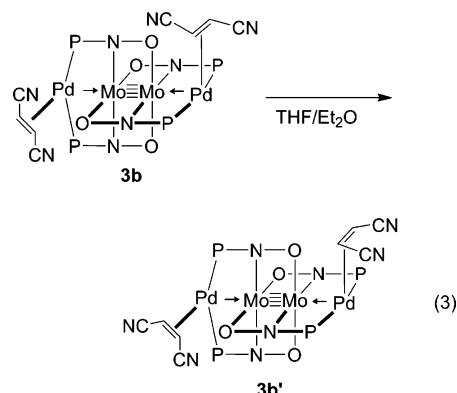
Figure 1. (a) Simulated and (b) observed $^{31}\text{P}\{^1\text{H}\}$ NMR spectra for **3n** in THF- d_8 at -40°C .

Raman spectral data of **3a–j** upon irradiation at 457.9 cm^{-1} showed a peak in the range of $388\text{--}404\text{ cm}^{-1}$ due to $\nu(\text{Mo–Mo})$. Among **3a–c**, the wavenumber of $\nu(\text{Mo–Mo})$ increased with an increase in the number of CN groups on the substrates, in the order of **3a** [389 cm^{-1} , comparable to that of **2** and tetrametal complexes $\text{Mo}_2\text{Pd}_2\text{X}_2(\text{pyphos})_4$ (**4a**: X = Cl; **4b**: X = Br; **4c**: X = I; $386\text{--}387\text{ cm}^{-1}$), having a triple-bond between Mo atoms and Pd–Mo single bonds] < **3b** (399 cm^{-1}) < **3c** [404 cm^{-1} , comparable to that of the quadruply bonded Mo_2 complexes such as **1** (394 cm^{-1}) and Pd(II) complexes, $\text{Mo}_2\text{Pd}_2\text{X}_4(\text{pyphos})_4$ (**5a**: X = Cl, **5b** = Br: 403 cm^{-1}), with no Mo–Pd bond].⁴⁰ 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 (vide infra).

The crystal structure of the tetracyanoethylene (TCNE) complex **3c** was previously described: TCNE coordinated an η^2 -olefin donor to each Pd(0) center.⁴⁴ We tried to crystallize the fumaronitrile adduct **3b** from a mixture of THF and ether, but its X-ray analysis, though its low quality



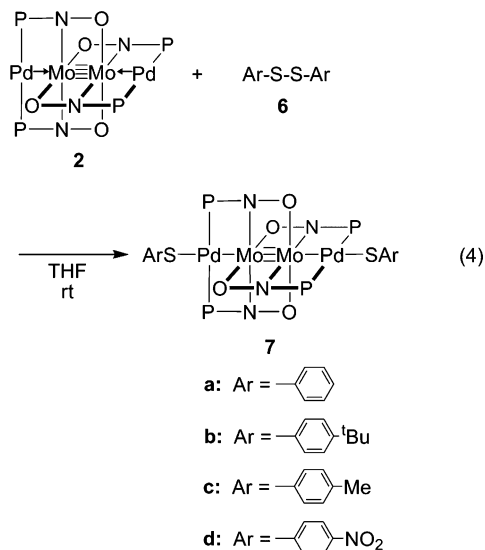
prevents precise discussion (details are given in Supporting Information), confirmed that the crystal was the **3b'** isomer, in which (*Z*)-1,2-dicyanoethylene coordinated to each palladium center, indicating that isomerization of fumaronitrile in **3b** to **3b'** proceeded during recrystallization (eq 3). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3b'** displayed a singlet at δ 25.2, slightly different from that of **3b** (δ 26.2), and the IR spectrum of **3b'** showed an absorption of $\nu(\text{CN})$ at 2220 cm^{-1} , distinguishable from that of **3b** (2213 cm^{-1}).



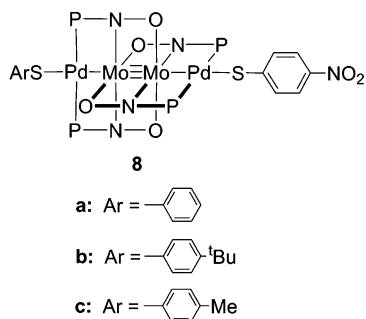
Reaction of Complex 2 with Diaryl Disulfides and Benzoyl Peroxide. Reaction of **2** with a slight excess amount of diaryl disulfides ArSSAr **6a–d** in THF at room temperature resulted in the formation of the corresponding 1,4-dithiolate tetrametal complexes $\text{Mo}_2\text{Pd}_2(\text{SAR})_2(\text{pyphos})_4$ (**7a**: Ar = C_6H_5 , **7b**: Ar = $4\text{-Me}_3\text{CC}_6\text{H}_4$, **7c**: Ar = $4\text{-MeC}_6\text{H}_4$, and **7d**: $4\text{-NO}_2\text{C}_6\text{H}_4$) (eq 4). Similar sulfide-adducts were reported for the reaction between the platinum analogue of complex **3** and diaryl disulfides.⁴⁷ Disulfides oxidatively added to a tetrametal skeleton in a formal 1,4-addition manner gave rise to the Pd(I) species. Such a reaction pattern is clearly different from that of the addition of diaryl disulfides to mononuclear transition metal complexes: diaryl disulfides react with mononuclear Pd(0) complexes to give a “Pd(SR)₂” species as an initial insertion step of the palladium-catalyzed addition of disulfides to various unsaturated bonds.⁴⁹ The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **7a–d** indicated a singlet signal around δ 19.0–20.1 because of the coordination of a phosphorus atom to the Pd(I) atoms. Moreover, the absorption spectra of **7a–d** exhibited an intense peak

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around 700 nm (698–718 nm) due to the MMCT band of the Pd–Mo σ -bond.⁴⁰



To gain insight into the mechanism of the 1,4-addition reaction of disulfides to **2**, we conducted the following controlled experiments: 0.5 equiv of **6b** and 0.5 equiv of **6d**, the latter of which was chosen because of the chemical shift difference between **7d** and other complexes **7a–c**, were added to a solution of **2** in THF at $-70\text{ }^\circ\text{C}$, and the reaction mixture was allowed to warm to room temperature *under dark conditions*. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum for the product of this reaction revealed the presence of three complexes, two homo dithiolate complexes **7b** and **7d**, and a new hetero dithiolate complex, $\text{Mo}_2\text{Pd}_2(\text{SC}_6\text{H}_4/\text{Bu})(\text{SC}_6\text{H}_4\text{NO}_2)(\text{pyphos})_4$ (**8b**), displaying two triplets at δ 18.8 and 20.4 with a small coupling constant (10 Hz) (Figure 2). The observed triplet pattern could be explained by coupling between two magnetically nonequivalent phosphorus nuclei bound to “Pd(SC₆H₄/Bu)” and “Pd(SC₆H₄NO₂)” moieties. Repeating the same operation, the addition of 0.5 equiv of each **6a** and **6d** and of **6c** and **6d** afforded the corresponding hetero dithiolate complexes **8a** and **8c** (Table 2). Such results strongly suggest that the mechanism involved a stepwise oxidation of **2**, as further supported by CV measurements (*vide infra*).



Treatment of **2** with benzoyl peroxide in THF at room temperature gave a green solution, from which a bis(benzoate) complex $\text{Mo}_2\text{Pd}_2(\text{PhCOO})_2(\text{pyphos})_4$ (**9**) was isolated as a whole product of the 1,4-oxidative addition of benzoyl peroxide to **2**. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **9** displayed a

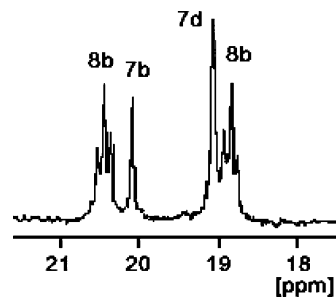


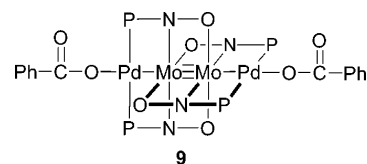
Figure 2. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of a hetero dithiolate complex **8b** (δ 18.8 and 20.4; triplets) along with homo dithiolate complexes **7b** (δ 20.1) and **7d** (δ 19.0).

Table 2. Selected Spectral Data for **7** and **8**

	$^{31}\text{P}\{^1\text{H}\}$ NMR	UV-vis	Raman
	δ /[ppm] ^a	λ_{max} /[nm] (ϵ /[M ⁻¹ cm ⁻¹]) ^b	ν /[cm ⁻¹] ^c
7a	19.8 (s)	704 (3.4×10^4)	388
7b	20.1 (s)	710 (1.4×10^4)	388
7c	20.0 (s)	711 (1.7×10^4)	388
7d	19.0 (s)	700 (3.4×10^4)	388
8a^d	20.2 (t, 10 Hz), 18.7 (t, 10 Hz)		
8b^d	20.4 (t, 10 Hz), 18.8 (t, 10 Hz)		
8c^d	20.2 (t, 10 Hz), 18.7 (t, 10 Hz)		

^a Measured in C₆D₆ at 35 °C. ^b Measured in THF at 35 °C. ^c $\nu(\text{Mo}—\text{Mo})$ by 457.9 nm laser excitation. ^d Not isolated.

singlet signal at δ 14.5, and the electronic absorption spectrum exhibited a maximum-absorption at 630 nm because of the formation of Pd–Mo bonds and underwent a greater blue shift than did that of the disulfide complexes **7a–d**. The IR spectrum of **9** exhibited absorbances due to $\nu_a(\text{COO})$ and $\nu_s(\text{COO})$ at 1554 and 1351 cm⁻¹, respectively, consistent with the terminal benzoyl groups.^{50,51}

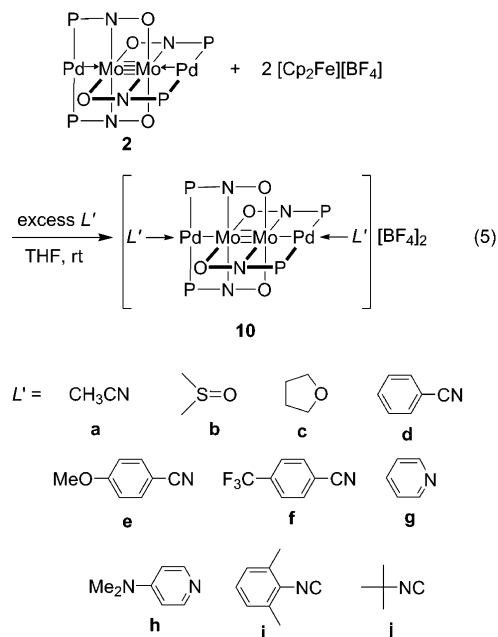


Chemical Oxidation of Complex 2. Chemical oxidation of **2** was performed in the presence of excess amounts of donor additives. Treatment of **2** with 2 equiv of [Cp₂Fe][BF₄] in acetonitrile resulted in the smooth formation of a green dicationic Pd(I) complex, [Mo₂Pd₂(pyphos)₄(CH₃CN)₂][BF₄]₂ (**10a**) (eq 5), in which acetonitrile coordinated to each Pd(I) center. The formulation of **10a** was confirmed by spectral data, conductivity, and elemental analysis.

Similarly, the oxidation of **2** using 2 equiv of [Cp₂Fe][BF₄] was performed in THF containing excess amounts of donor molecules to afford dicationic Pd(I) complexes [Mo₂Pd₂(pyphos)₄(L')₂][BF₄]₂ (**10b**; L' = dimethylsulfoxide, **10c**: L' = THF, **10d**: L' = benzonitrile, **10e**: L' = *p*-methoxyphenylnitrile, **10f**: L' = *p*-trifluoromethylphenylnitrile, **10g**: L'

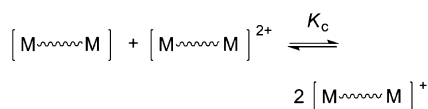
(50) (a) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part B: Applications in Coordination, Organometallic, and Bioinorganic Chemistry*, 5th ed.; John Wiley & Sons, Inc.: New York, 1997. (b) Silverstein, R. M.; Webster, F. X. *Spectrometric Identification of Organic Compounds*, 6th ed.; John Wiley & Sons, Inc.: New York, 1998. (c) Canty, A. J.; Denney, M. C. *Organometallics* **2004**, *23*, 1122.

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= pyridine, **10h**: $L' = p$ -dimethylaminopyridine). Isonitrile complexes $[\text{Mo}_2\text{Pd}_2(\text{pyphos})_4(\text{CNXyl})_2][\text{BF}_4]_2$ (**10i**) and $[\text{Mo}_2\text{Pd}_2(\text{pyphos})_4(\text{CN}^t\text{Bu})_2][\text{BF}_4]_2$ (**10j**) were obtained by oxidation of the isonitrile-Pd(0) complexes **3h** and **3i**, respectively. All complexes were characterized by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR and IR spectroscopy, solution conductivity, and combustion analysis. Because of the MMCT band between Pd(I) and Mo(II), the color of all complexes was intense green ($\lambda_{\text{max}} = 602\text{--}706$ nm, Table 3). Chemical shift values of the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra for **10b–j** and their Raman spectral data suggested the presence of Pd(I) centers (Table 3). IR spectra of isonitrile complexes **10i** (2160 cm^{-1}) and **10j** (2190 cm^{-1}) were shifted to a higher wavenumber compared to the corresponding Pd(0) complexes **3h** (2060 cm^{-1}) and **3i** (2105 cm^{-1}), reflecting the decreased electron density at the Pd(I) metal which weakened the π -back-donation from metal to isonitrile ligands.

Electrochemical Studies. Electrochemistry has been used for evaluating electronic communication between redox-active metal centers. A conproportionation equilibrium constant, K_c , can be estimated from the separation between two oxidation potentials in cyclic voltammetry.⁵²



$$\text{where } K_c = \exp\left(\frac{\Delta E_{1/2} \text{ (in mV)}}{25.69}\right)$$

According to the definition by Robin and Day for mixed-valence compounds, electronic coupling is classified into three classes depending on the magnitude of K_c : if there is no communication between the two metal centers, K_c is small (<100) (Class I); if there is full electron delocalization between the metal centers, K_c is very large ($\geq 10^6$) (Class

Table 3. Selected Spectral and Electrochemical Data for **10**

	$^{31}\text{P}\{^1\text{H}\}$ NMR	UV-vis	Raman		CV
			δ /[ppm] ^d	λ_{max} /[nm] (ϵ /[M ⁻¹ cm ⁻¹]) ^b	
10a	14.5 (s)	681 (1.9×10^4)	389	-225, -440 (215)	4.3×10^3
10b	13.6 (s)	684 (2.4×10^4)	388	-220, -435 (215)	4.3×10^3
10c	14.5 (s)	706 (2.3×10^4)	390	-285, -455 (170)	7.5×10^2
10d	13.7 (s)	636 (3.5×10^4)	390	-195, -430 (235)	9.4×10^3
10e	13.7 (s)	630 (3.7×10^4)	391	-255, -435 (180)	1.1×10^3
10f	13.6 (s)	683 (2.7×10^4)	390	-270, -430 (160)	5.1×10^2
10g	16.1 (s)	604 (6.9×10^4)	388	-325 ^e	—
10h	17.0 (s)	602 (9.0×10^4)	388	-490 ^e	—
10i	16.5 (s)	613 (4.6×10^4)	389	-460 ^e	—
10j	16.6 (s)	602 (6.7×10^4)	391	-595 ^e	—

^a Measured in CD_3OD at 35°C except for **10a**, which was measured in CD_3CN . ^b Measured in CH_2Cl_2 . ^c $\nu(\text{Mo-Mo})$ by 457.9 nm laser excitation. ^d Measured in THF containing 0.1 M $^t\text{Bu}_4\text{NBF}_4$, Pt disk working electrode, Ag/Ag⁺ reference electrode, Pt wire counter-electrode, scan rate 100 mV s^{-1} . ^e An irreversible oxidation wave.

III); the intermediate situation in which there is electronic coupling but not complete delocalization is defined as Class II, where $100 < K_c < 10^5$.⁵³ Cyclic voltammetry of **2** in acetonitrile and THF in the presence of 0.1 M $^t\text{Bu}_4\text{N}^+[\text{BF}_4]^-$ using a scan rate of 100 mV s^{-1} , revealed two reversible oxidation processes due to the oxidation of terminal Pd centers and the two waves were observed at -490 and -650 mV versus Ag/Ag⁺ ($\Delta E_{1/2} = 160$ mV) in acetonitrile (Figure 3) and -200 and -415 mV versus Ag/Ag⁺ ($\Delta E_{1/2} = 215$ mV) in THF, corresponding to K_c of 5.1×10^2 and 4.3×10^3 , respectively. According to the Robin and Day definition, these values are within those of the Class II, indicating that both terminal Pd centers communicated through the Mo₂ unit. The first one-electron oxidation occurred at one of two palladium centers to result in the spontaneous formation of a Mo-Pd single bond, which caused the bond-order reduction of the Mo₂ unit from four to three to interact with the remaining Pd(0) center. The electronic delocalization among the four metal array may be affected by the axial coordination of donor molecules, acetonitrile, and THF, respectively. On the basis of these experimental results, it is likely assumed that the reactions of **2** with disulfides and benzoylperoxide proceeded by a stepwise oxidation mechanism involving the mixed-valenced species (Scheme 1).

This is suggested by the electrochemistry of **10** as well. Cyclic voltammetry of **10a–j** revealed that the profile of Pd(0) was highly dependent on axial donor molecules. As summarized in Table 3, we observed two types of redox

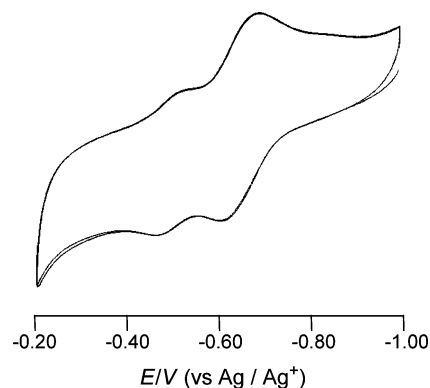
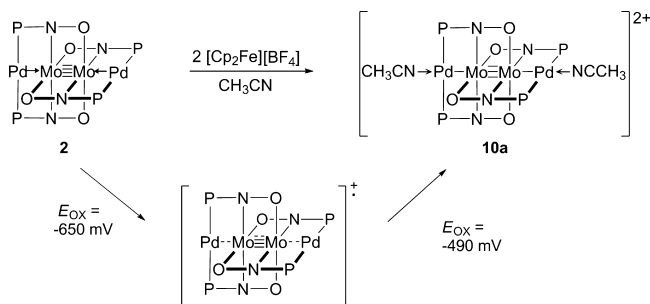


Figure 3. Cyclic voltammogram of **2** recorded in 0.1 M acetonitrile solution of $^t\text{Bu}_4\text{N}^+[\text{BF}_4]^-$ at a scan rate 100 mV s^{-1} .

(52) Richardson, D. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 1278.

Scheme 1

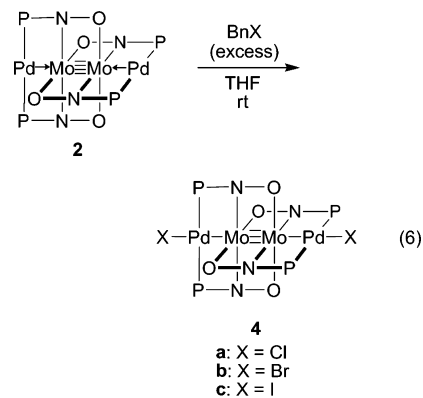


categorized as follows: complexes **10a–f** showed two waves attributed to electron communication, whose K_c lies in the range of Class II, and **10g–j** showed one wave. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **10a–f** displayed a singlet around δ 13.6–14.5, whereas that of **10g–j** showed a singlet around δ 16.1–17.0. Thus, the σ -donating ligand increased electron density at Pd(I) atom. These observations are consistent with the known evidence that the metal–metal bonding nature of paddlewheel-type dinuclear complexes are sensitive to axial ligands.^{54,55} This is a rare example of metal centers communicating through another metal unit,⁵⁶ suggesting that the reaction of **2** with diaryl disulfides, benzoyl peroxide, and $[\text{Cp}_2\text{Fe}][\text{BF}_4]$ proceeded through this electronic communication to afford the corresponding Pd(I) complexes.

Reaction of Complex 2 with Alkyl and Aryl Halides.

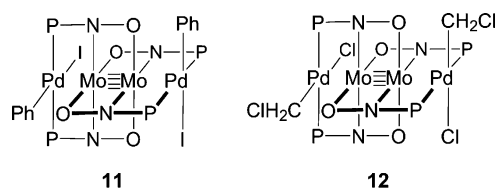
Oxidative addition of alkyl and aryl halides to **2** gave two types of reaction products; a Pd(I) species through the same mechanism as described above and a Pd(II) species, depending on the substrates and reaction conditions. We first examined the reaction of **2** with benzyl halides BnX (X = Cl, Br, I). Treatment of **2** with excess amounts of BnX (X = Cl, Br, I) in THF smoothly afforded the corresponding Pd(I) complexes **4a–c** accompanied by bibenzyl $\text{PhCH}_2\text{CH}_2\text{Ph}$ (eq 6). These reactions are categorized as the same type as that of **2** with disulfide and benzoyl peroxide. In this reaction, we did not observe any intermediate benzyl-Pd species such as $\text{PhCH}_2\text{-Pd-Mo-Mo-Pd-X}$ and $\text{PhCH}_2\text{-Pd-Mo-Mo-Pd-CH}_2\text{Ph}$, though the similar 1,4-oxidative addition of CH_3I and CH_2Cl_2 to $[\text{Mo}_2\text{Ir}_2(\text{pyphos})_4(\text{CNR})_4]^{2+}$ complexes resulted in the selective formation of tetrametal complexes bearing the dissymmetric frameworks $\text{CH}_3\text{-Ir-Mo-Mo-Ir-I}$ and $\text{ClCH}_2\text{-Ir-Mo-Mo-Ir-Cl}$, respectively.⁴⁶ This might be a result of the ready reaction of the highly reactive benzyl halides with any “ PhCH_2Pd ” species to give **4a–c** together with the formation of bibenzyl, consistent with the reaction of mononuclear Pd(0) complexes with benzyl halides.^{57,58}

In the reaction of **2** with phenyl halides PhX (X = Cl, Br, I) as typical substrates with a $\text{C}(\text{sp}^2)\text{-X}$ bond, we observed



the same reaction pattern as shown in eq 5. The reactivity of phenyl halides toward oxidative addition to $\text{Pd}(\text{PPh}_3)_4$ was reported in the order of $\text{PhI} > \text{PhBr} \gg \text{PhCl}$,^{59,60} and this tendency was observed in the reaction of **2** as well. Reaction of **2** with 2 equiv of PhI in THF at ambient temperature for 12 h gave **4c** and biphenyl in quantitative yield. The reaction of **2** with excess amounts of PhBr in THF at room temperature for 12 h afforded **4b** in 90% yield, whereas the reaction of **2** with PhCl required reflux condition of chlorobenzene,²⁰ resulting in the formation of **4a** in 77% yield over 12 h.

In sharp contrast to the reaction of **2** with 2 equiv of PhI, the reaction of **2** with excess amounts of PhI in THF resulted in the formation of another complex $\text{Mo}_2\text{Pd}_2(\text{Ph})_2\text{I}_2(\text{pyphos})_4$ (**11**) together with trace amount of **4c**. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **11** displayed a singlet signal at δ 16.2 assignable to phosphorus atoms bound to the Pd(II) species bearing one phenyl and one iodo ligand, though its chemical shift value was almost the same as that [δ 16.5 (s)] of **4c**.⁶¹ The absorption spectrum of **11** showed a broad shoulder peak around 450 nm, which was comparable to that (482–486 nm) found for Pd(II) complexes **5a,b** but different from that (707 nm) of **4c**, indicating that complex **11** has no bonding interaction between the two Pd(II) atoms and the Mo_2 unit. Raman spectrum of **11** showed an absorption due to $\nu(\text{Mo-Mo})$ at 398 cm^{-1} , the value of which is comparable to that found for the quadruply bonded Mo_2 unit. A similar reaction pattern was reported for the reaction of **2** with dichloromethane, resulting in the slow crystallization of $\text{Mo}_2\text{Pd}_2(\text{CH}_2\text{Cl})_2(\text{Cl})_2(\text{pyphos})_4$ (**12**), which was a product of 1,1',4,4'-addition of two dichloromethane with two Pd(0) centers activated through interaction with the Mo_2 core, in 67% yield as red crystals of a pair of enantiomeric isomers determined by X-ray analysis.⁴⁴ Until now, we were not able to obtain clear evidence that the reason why the reaction of **2** with PhI to produce two different products was sensitive to the amount of PhI.



When complex **2** was treated with excess amounts of CH_3I in THF, we obtained a new product, $\text{Mo}_2\text{Pd}_2(\text{CH}_3)_2\text{-}$

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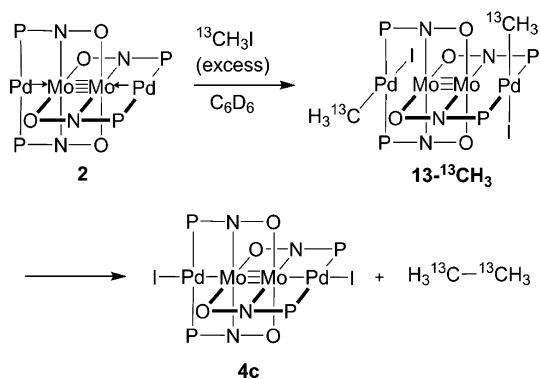
(55) Kawamura, T.; Maeda, M.; Miyamoto, M.; Usami, H.; Imaeda, K.; Ebihara, M. *J. Am. Chem. Soc.* **1998**, *120*, 8136.

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Scheme 2



(I)₂(pyphos)₄ (**13**), along with a small amount of **4c**. In the ¹H NMR spectrum of **13**, protons of the methyl group bound to the Pd moiety were observed as a triplet at δ 1.42 with a coupling constant of $J_{\text{PH}} = 5.7$ Hz. Reaction of **2** with enriched ¹³CH₃I afforded the corresponding enriched product **13**-¹³CH₃, whose ¹H NMR spectrum afforded a methyl signal as a doublet of triplet because of the coupling constants of $J_{\text{CH}} = 138$ Hz and $J_{\text{PH}} = 5.7$ Hz, and the ¹³C NMR spectrum displayed the Pd-CH₃ signal at δ 19.4 as a quartet ($J_{\text{CH}} = 138$ Hz) with a correlation to the proton signal of the methyl group in the ¹³C-¹H HETCOR spectrum, indicating clearly that the methyl group was bound to the palladium atom supported by the two pyphos ligands. It is curious that there was no coupling between the C nuclei of the CH₃ moiety and two phosphorus atoms of the pyphos ligands, though similar phenomena were observed in the NMR spectra of the Mo₂Ir₂ complex [Mo₂Ir₂(¹³CH₃)(I)(XylNC)₄(pyphos)₄](Cl)₂.⁴⁶ The ³¹P{¹H} spectrum of **13** in C₆D₆ displayed two signals at δ 27.8 and 27.6, almost the same chemical shift values of **12** and with a similar pattern.⁴⁴ A dinuclear Pd(0) complex Pd₂(μ -dppm)₃, in which two Pd(0) centers attractively interact, reacted with CH₂X₂ (X = Cl, Br, I) to give the corresponding Pd(II) complexes having a methylene-bridged, X-Pd-CH₂-Pd-X framework.¹⁹ In contrast, because two Pd(0) centers of **2** are placed at axial positions of the Mo₂ core, the reaction of **2** with excess amounts of PhI, CH₂Cl₂, and CH₃I afforded a Pd(II) species in a 1,1',4,4'-addition manner.

Moreover, NMR studies of the reaction of **2** with 10 equiv of ¹³CH₃I indicated the formation of Pd(I) species **4c** along with ethane (¹³CH₃-¹³CH₃) through the formation of **13**-¹³CH₃ (Scheme 2). Such reactivity is in sharp contrast to the fact that [Mo₂Ir₂(CH₃)(I)(RNC)(pyphos)₄](Cl)₂ did not react further with CH₃I.⁴⁶ Prolonged heating of **12** in dichloromethane resulted in the formation of **5a**. In the case of **13**, we detected **4c** as a whole product (Scheme 2) because **4c** is thermally stable, and the iodo analogue of **5a** is thermally too unstable to be converted to **4c**.⁴⁰

Furthermore, UV-vis spectra of **13** clearly showed the conversion of **13** to **4c**; decreasing the absorption around 450 nm due to **13** with increasing a peak at 707 nm due to **4c**. Thus, the Pd-CH₃ bond in **13** was cleaved, while the Pd-Ph bond of **11** was not cleaved under UV-vis irradiation (Figure 4).

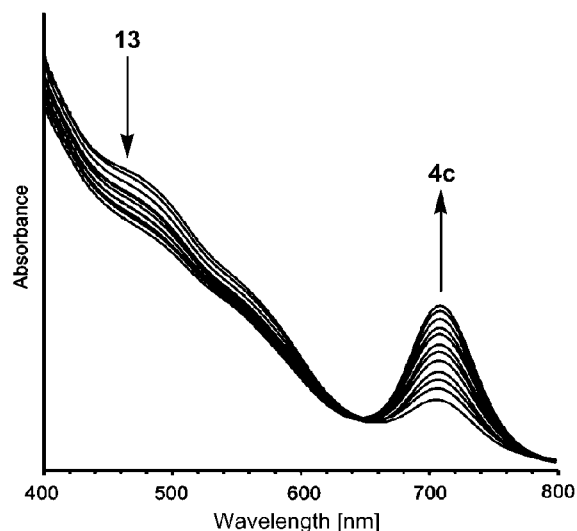


Figure 4. UV-vis spectral changes of **13** in THF with respect to time for time = 0–55 min.

Conclusion

The quadruply bonded-dimolybdenum complex Mo₂(pyphos)₄ (**1**) acted as a core part in the construction of Mo₂Pd(0)₂ tetranuclear array of Mo₂Pd₂(pyphos)₄ (**2**) through the reaction of **1** with a Pd(0) source. Highly unsaturated Pd(0) centers in **2** showed high reactivity toward disulfides and benzoyl peroxide to give the corresponding 1,4-oxidative added Pd(I) complexes. In such reactions, we observed a unique function of the Mo₂ moiety, which attractively interacted with each Pd(0) atom, not only compensating for the unsaturation but also electrochemically communicating between the two Pd centers to proceed in a stepwise oxidation of the two Pd(0) centers through mixed-valenced tetrametal species. The electronic communication is assumed to be an important process in the mechanism of the reaction of **2** with diaryl disulfides, benzoyl peroxide, and [Cp₂Fe][BF₄]. Thus, clusters involving tunable metal-metal bonds are not simply an extension of mononuclear Pd(0) complexes. The reaction of **2** with alkyl and aryl halides led to the formation of Pd(I) and Pd(II) complexes depending on the reaction conditions and substrate type. We are currently studying the reactivity and selectivity of these multimetal clusters.

Acknowledgment. We are grateful for financial support from the Ministry of Education, Culture, Sports, Science and Technology. A.S. thanks JSPS for supporting her scholarship (2006–2009).

Supporting Information Available: Detailed experimental procedures and analytical and spectral data for complexes, the VT-¹H NMR spectra of **3n**; the Eyring plot of $\ln(k/T)$ versus $1/T$ for **3n**; a CIF file and details of X-ray analysis for complex **3b'**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(61) The evidence for phenyl groups bound to the Pd(II) atoms in **12** was derived from the ³¹P{¹H} NMR spectra for the reaction product upon treating **2** with various *p*-X-C₆H₄I (X = F, Cl, MeO, NO₂, CN), whose chemical shift values are linearly correlated to Hammett σ_p .