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# Preparation and Properties of 1,2-Diferrocenyl-Substituted 3,4-Diphosphinidenecyclobutenes and Their Complexes: The First Application of a Diphosphinidenecyclobutene Unit as a Linker of Functional Moieties

Subaru Kawasaki, Akitake Nakamura, Kozo Toyota, and Masaaki Yoshifuji*

*Department of Chemistry, Graduate School of Science, Tohoku University, Aoba, Sendai 980-8578, Japan*

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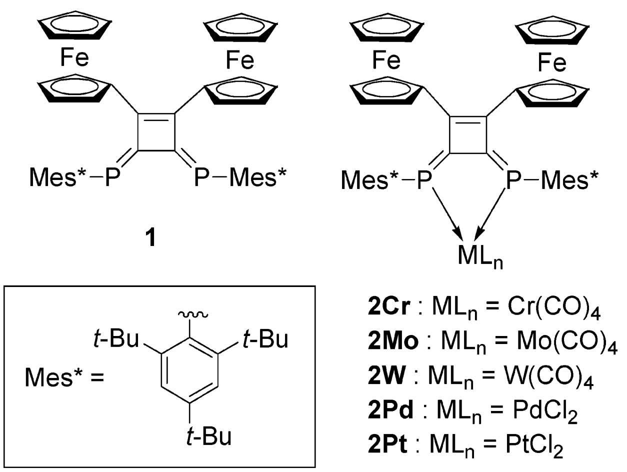
Compounds with two ferrocenyl units connected with 3,4-diphosphinidenecyclobutene (DPCB) linkers at the 1,2-positions (**1**) and their transition metal chelate complexes (**2**) were prepared, and the spectroscopic and electrochemical properties were studied. The compounds were examined by cyclic voltammetry, and $\Delta E_{1/2}$ values (the separation between successive $Fe^{2+}/Fe^{3+}$ oxidation potentials) were determined. Being fully conjugated with DPCB linkers, those compounds demonstrated electrochemical communication: the $Cr(CO)_4$ complex of **1** (**2Cr**) showed a strong interaction ($\Delta E_{1/2}$ = 350 mV), whereas $PdCl_2$ and $PtCl_2$ complexes of **1** (**2Pd** and **2Pt**) displayed a decreased interaction compared to that of **1**.

## Introduction

3,4-Diphosphinidenecyclobutenes (DPCB)[1] possess unique structures containing $sp^2$ phosphorus atoms and work as bidentate ligands to transition metals. We have studied the structures and the coordination nature of DPCB derivatives.[1c] In addition, we have applied DPCB ligands to Pd-, Pt-, and Cu-catalyzed reactions.[2] Although the DPCB molecules are bidentate ligands with conjugated flat structures, there has been no report on the application utilizing the characteristic nature of their $\pi$-systems. Taking the unique character of the DPCB molecule into account, a molecular device with the DPCB moiety is expected to possess interesting physical properties of DPCB derivatives.

Among the possible approaches to molecular devices, studies on the construction of multiredox systems and the understanding of electronic communication are interesting subjects for developing new electronic materials and devices.[3] One approach to construction of multiredox systems is to utilize molecules that contain redox center(s) and conjugated linkers.[4] For example, ferrocenes connected via alkene or benzene linkers are promising. Since the preparation of the Creutz−Taube ion,[5] studies of molecules where two or more metal centers are linked by a bridging ligand with pronounced electronic interactions have been of interest.

**Chart 1. Compounds 1 and 2**



Here we report the syntheses and properties of a 1,2-diferrocenyl-substituted DPCB derivative (**1**) and its transition metal complexes **2** (Chart 1) as the first attempted application of DPCB as a linker of functional moieties. The DPCB **1** exhibited two reversible oxidation waves in cyclic voltammetry, indicating electronic interaction between the two iron centers. The transition metal complexes **2** showed a shift of the oxidation waves,

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* To whom correspondence should be addressed. E-mail: yoshifj@mail.tains.tohoku.ac.jp.

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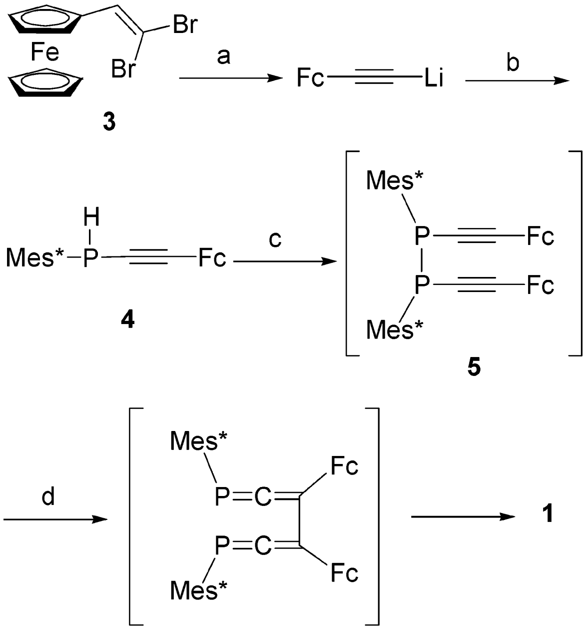
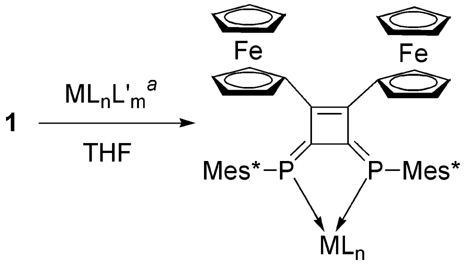
10.1021/om0500772 CCC: \$30.25

**Scheme 1. Synthesis of 1**[a]



[a] Reagent and conditions: (a) *n*-BuLi (2 equiv), THF, −78 °C. (b) Mes*P(H)Cl, THF, rt. (c) *n*-BuLi (1 equiv), THF, −78 °C, 10 min; then 1,2-dibromoethane (0.5 equiv), −78 °C, 10 min; rt, 1 h. (d) PhMe, reflux, 30 min. Fc = ferrocenyl.

**Scheme 2. Synthesis of Transition Metal Complexes of 1**[a]



[a] ML$_n$L′$_m$ = (*nor*-$C_7H_8$)M(CO)$_4$ (for **2Cr**, **2Mo**, and **2W**); ML$_n$L′$_m$ = $PdCl_2(MeCN)_2$ (for **2Pd**); ML$_n$L′$_m$ = $PtCl_2(PhCN)_2$ (for **2Pt**).

indicating that electronic interactions between the two iron centers might be controlled. The control of redox activities using transition metals will attract interest in inorganic and organic materials chemistry.[6]

## Results and Discussion

**1. Preparations of Diferrocenyldiphosphinidenecyclobutene and Its Complexes.** Scheme 1 shows the synthesis of **1**: Ferrocenylethynyllithium was generated in situ from dibromoalkene **3** by Corey−Fuchs reaction[7] using 2 equiv of *n*-BuLi and was allowed to react with Mes*P(H)Cl[8] (Mes* = 2,4,6-*tert*-$Bu_3C_6H_2$) to give the corresponding (ferrocenylethynyl)phosphine **4**. Deprotonation of **4** with *n*-BuLi in THF at −78 °C followed by treatment with 1,2-dibromoethane and refluxing in toluene gave the desired diphosphinidenecyclobutene **1**, via intermediates **5** and **6**, in 64% yield based on **4**.

**Table 1. $^{31}$P NMR (162 MHz) Data for 1 and 2**

| | 1 | 2Cr | 2Mo | 2W | 2Pd | 2Pt |
|---|---|---|---|---|---|---|
| $\delta_P$[a] | 154.2 | 170.0 | 153.4 | 132.9[b] | 134.9 | 111.4[c] |

[a] Measured in $CDCl_3$. [b] Satellite, $^1J_{PW}$ = 256.6 Hz. [c] Satellite, $^1J_{PPt}$ = 4486.0 Hz.

Transition metal complexes of **1** were then prepared as shown in Scheme 2. When **1** was allowed to react with $PdCl_2(MeCN)_2$ in THF at room temperature, the reaction proceeded to give **2Pd** almost quantitatively. Although the reaction of **1** with $PtCl_2(PhCN)_2$ was slow in THF at room temperature, heating of the mixture at 50 °C for 5 h led to the formation of platinum complex **2Pt** (52% yield). Complexes of group 6 transition metals, **2Cr**, **2Mo**, and **2W**, were also prepared, using (norbornadiene)M(CO)$_4$ (M = Cr, Mo, W).

**2. Spectroscopic Properties.** The $^{31}$P NMR data for **1** and **2** are listed in Table 1. Platinum complex **2Pt** appeared at $\delta_P$ 111.4 with characteristic satellite signals, and tungsten complex **2W** appeared at $\delta_P$ 132.9 with satellite signals. It should be noted that the heavier metal causes a shift to a higher field in the case of group 6 and 10 metal complexes of other DPCB derivatives.[9]

The $^1$H NMR spectra of **1** and **2** showed some interesting features (see Supporting Information, Figures S1−S6, S7a−d, and S8a−g). In the case of **1**, the *o-tert*-butyl protons ($\delta$ 1.60−1.65) and the protons in the Cp ring ($\delta$ 4.0−4.3) adjacent to the DPCB appeared as broad signals in $CDCl_3$ at room temperature (Figure S1). In contrast, the corresponding signals of complexes **2** appeared as sharp signals, especially in the cases of **2Pd** (Figure S5) and **2Pt** (Figure S6), in $CDCl_3$ at room temperature. In the cases of the $^1$H NMR spectra of **2Cr**, **2Mo**, and **2W** (Figures S2−S4), relatively sharp signals, compared with those of **1**, were observed.

To clarify the reasons for the broadening of the signals, variable-temperature $^1$H NMR studies of **1** and **2Pd** were carried out (Figures S7a−d and S8a−g), and we found that conformational change of the bulky ferrocenyl substituents and the cyclobutene ring in the NMR time scale caused the broadening of the signals at room temperature.[10] These signals of **1** become sharp as the temperature increases in toluene-$d_8$ (Figure S7a−d). At room temperature in toluene-$d_8$, signals due to protons of the Cp ring adjacent to the DPCB are unclear, while the *o-tert*-butyl protons appear as a broad signal (Figure S7a). At 80 °C, the *o-tert*-butyl protons appear as a sharp singlet ($\delta$ 1.69), and the Cp ring protons

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(10) Attempted crystallographic analysis of compounds **1** and **2** failed, because of lack of suitable single crystals for X-ray analysis.

**Chart 2. Schematic Conformation of 1**

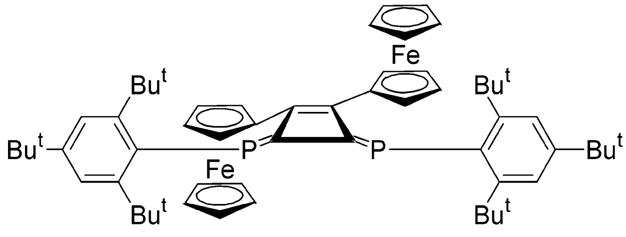
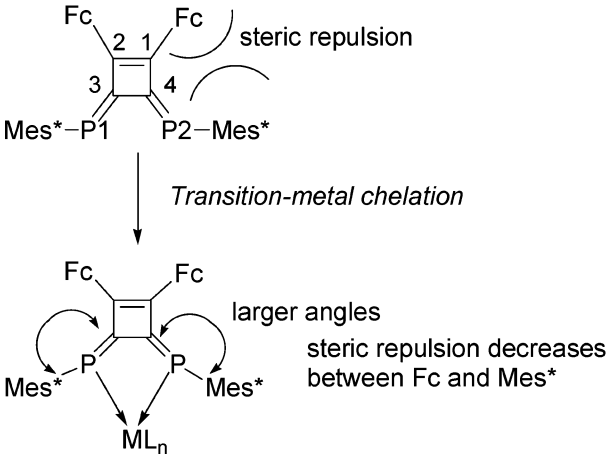


**Chart 3. Schematic Chelation Effect on DPCB Complexes**



adjacent to the DPCB become detectable ($\delta$ 4.0–4.3) (Figure S7d).

In the case of **2Pd**, these signals become broad with *decreasing* temperature in $CD_2Cl_2$ (Figure S8a–g). At −40 °C, both the *o-tert*-butyl protons and the *m*-Mes* protons appear as broad split signals (Figure S8d). At −80 °C, these signals appear as sharp inequivalent signals [Figure S8f, $\delta$ 1.53 and 1.77 (*o-tert*-Bu), $\delta$ 7.56 and 7.72 (*m*-Mes*)]. At this temperature, the Cp ring protons adjacent to the DPCB appear as four inequivalent signals at $\delta$ 2.26, 4.15, 4.56, and 5.17.

These changes in the $^1$H NMR spectra are explicable as follows. In the case of **1**, one bulky ferrocenyl group is located above the cyclobutene ring and the other is located below the cyclobutene ring due to steric congestion between the ferrocenyl groups and *o-tert*-butyl groups of the Mes* groups (Chart 2), similarly to the case of the 1,2-diphenyldiphosphinidenecyclobutene derivative[1d] in the crystal, and conformational exchange occurs slowly in solution at room temperature on the NMR time scale. When the temperature increases, the positional exchange occurs faster and this makes the signals sharp, as shown in Figure S7b–d.

In the case of the complex **2Pd**, the steric congestion between the ferrocenyl substituents and the *o-tert*-butyl groups is released by complex formation, because chelation makes the C(3)=P(1)–C(*ipso*) and C(4)=P(2)–C(*ipso*) angles larger (Chart 3) and the Mes* group moves away from the ferrocenyl group.[11] Consequently, those signals become sharp. It is worth noting that these dynamics changes caused by the metal chelation on the NMR time scale were first observed in our DPCB systems.

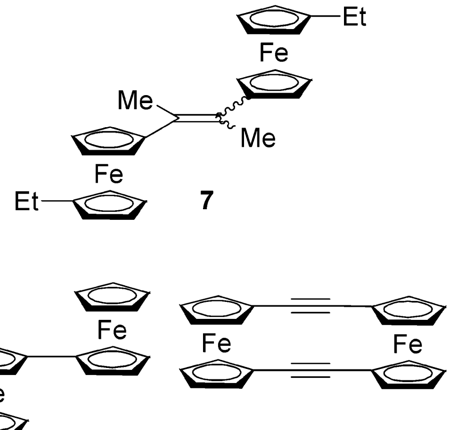
In addition, a charge delocalization to the planar DPCB moiety was indicated by UV–vis spectra: absorbance of **1** at 523 nm shifted to a longer wavelength by complex formation (573 nm for **2Pd**, 556 nm for **2Pt**, 532 nm for **2Mo**, 543 nm for **2W**). This tendency is also valid in the case of **2Cr**: Although the corresponding absorption band of **2Cr** appeared as a shoulder ($\lambda_{max}$ was unclear), comparison of the spectrum of **2Cr** with that of **1** indicated the red-shift for **2Cr**.

**Table 2. CV Data for 1 and 2[a]**

| compound | $E_{1/2}(1)$/V | $E_{1/2}(2)$ or $E_p$/V[b] | $E_{1/2}(3)$ or $E_p$/V[b] | $\Delta E_{1/2}$/V[c] | $K_c$ |
|---|---|---|---|---|---|
| **1** | 0.23 | 0.48 | | 0.25 | $2.0 \times 10^4$ |
| **2Cr** | 0.21 | 0.56 | (0.96) | 0.35 | $1.0 \times 10^6$ |
| **2Mo** | 0.24 | (0.63) | (0.97) | | |
| **2W** | 0.20 | (0.66) | (0.89) | | |
| **2Pd** | 0.45 | 0.64 | | 0.19 | $1.8 \times 10^3$ |
| **2Pt** | 0.41 | 0.62 | (1.37) | 0.21 | $4.1 \times 10^3$ |

[a] Cyclic voltammograms were recorded in $CH_2Cl_2$ containing 0.1 M *n*-$Bu_4NClO_4$. [b] Data in parentheses are irreversible waves ($E_p$). [c] $\Delta E_{1/2} = E_{1/2}(2) - E_{1/2}(1)$.

**Chart 4. Compounds 7–10**



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**3. Electrochemical Properties.** The cyclic voltammogram of **1** in $CH_2Cl_2$ (1 mM, *n*-$Bu_4NClO_4$, 30 mV/s) exhibited two reversible oxidation waves at 0.23 and 0.48 V (Table 2). The $\Delta E_{1/2}$ values (250 mV) reflect a considerable electronic interaction between the iron centers through the DPCB linker. This interaction is larger than that of (*E*)- or (*Z*)-1,2-bis(1′-ethyl-1-ferrocenyl)-1,2-dimethylethylene, **7** (Chart 4, $\Delta E_{1/2}$ = 150 mV, in MeCN with 0.1 M *n*-$Bu_4NBF_4$).[12,13] Chelation of metals may perturb the interaction between the two ferrocenyl groups. We thus investigated electrochemical properties of **2**. The cyclic voltammogram of **2Cr** in $CH_2Cl_2$ (1 mM, *n*-$Bu_4NClO_4$, 30 mV/s) exhibited two reversible oxidation waves (0.21 and 0.56 V) and one irreversible oxidation wave (0.96 V). The reversible waves presumably correspond to oxidation at the two ferrocenyl centers, by comparison with the results of **1**, while the irreversible wave is attributable to the $Cr^{0/1+}$ oxidation,[14] although some factors such as medium effects should be taken into account.[4i,15] The results indicate that chelation of Cr affects the second oxidation poten-

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[11] This type of changes in angles were observed in our previous crystallographic studies of some DPCB ligands and their complexes. For example, in the case of seven-membered-ring-fused DPCB derivative, the C=P–C angles change from 99.6(2)° and 100.4(2)° (av 100.0°) to 114.1(4)° and 118.2(4)° (av 116.2°) (ref 1b).

[12] Dong, T.-Y.; Ke, T.-J.; Peng, S.-M.; Yeh, S.-K. *Inorg. Chem.* **1989**, *28*, 2103.

[13] Strictly speaking, comparison of the $\Delta E_{1/2}$ values should be carefully made taking the difference of CV conditions, such as solvent and electrolyte, into account.

tial $E_{1/2}(2)$ rather than the first oxidation potential $E_{1/2}(1)$ (probably, **2Cr**$^{2+}$ is less stable than **1**$^{2+}$, while stabilities of **2Cr**$^{+}$ and **1**$^{+}$ are similar). Consequently, the electronic interaction of **2Cr** becomes very large [$\Delta E_{1/2} = 350$ mV; $\Delta E_{1/2} = E_{1/2}(2) - E_{1/2}(1)$] and comparable to those of biferrocene **8** ($\Delta E_{1/2} = 350$ mV, in $CH_2Cl_2$ with 0.2 M $n$-$Bu_4NBF_4$) and bisacetylene-bridged ferrocenophane **9** ($\Delta E_{1/2} = 355$ mV, in $CH_2Cl_2$ with 0.2 M $n$-$Bu_4NBF_4$).[13,16]

This tendency is also observed in the cases of **2Mo** and **2W**, although the second oxidation potential appeared to be irreversible. The cyclic voltammogram of **2Mo** exhibited one reversible oxidation wave (0.24 V) and two irreversible waves (0.63 and 0.97 V). Similarly, CV for **2W** exhibited one reversible oxidation wave (0.20 V) and two irreversible waves (0.66 and 0.89 V). Again, the group 6 neutral M(0) metal in the $M(CO)_4$ moiety affects the second oxidation potential rather than the first oxidation potential.

On the other hand, chelation of group 10 M(II) metal in the $MCl_2$ moiety affected both $E_{1/2}(1)$ and $E_{1/2}(2)$ oxidation potentials: the cyclic voltammogram of **2Pd** and **2Pt** exhibited two reversible oxidation waves (0.45 and 0.64 V for **2Pd**; 0.41 and 0.62 V for **2Pt**) and one irreversible reduction wave attributable to the Pd or Pt center (−1.06 and −1.47 V, respectively). As the DPCB−group 10 metal(II) complexes are likely to be more electron deficient than the DPCB−group 6 metal(0) complexes, the first oxidation of the ferrocenyl units of **2Pd** and **2Pt** will be more difficult than that of the DPCB−group 6 metal carbonyl complexes.

The effect of the metal center on the second oxidation wave in both the group 6 metal complexes and the group 10 metal complexes is explicable as follows: a positive charge generated by oxidation of the ferrocenyl unit delocalizes to the cyclobutene ring and the metallacycles. This delocalization onto the metallacycles makes the second oxidation reluctant.

The $\Delta E_{1/2}$ values found for the redox processes reflect a large degree of electronic interaction between the iron centers through the DPCB moiety. The equilibrium constant, $K_c$,[5b] for the comproportionation reaction shown in eq 1 is given by eq 2, where FcDPCB is diferrocenyldiphosphinidenecyclobutene **1**. In many cases, $\Delta E°$ can be estimated from $\Delta E_{1/2}$.[5c]

$$[\mathrm{FcDPCB}] + [\mathrm{FcDPCB}^{2+}] \rightleftharpoons 2[\mathrm{FcDPCB}^{+}] \quad (1)$$

$$K_c = [\mathrm{FcDPCB}^{+}]^2/[\mathrm{FcDPCB}][\mathrm{FcDPCB}^{2+}] = \exp[\Delta E°(F/RT)] \quad (2)$$

where $F$ is the Faraday constant, $R$ is the gas constant, and $T$ is the temperature, in K.

The calculated $K_c$ values were as follows, assuming $\Delta E° \cong \Delta E_{1/2}$: **1**$^{+}$ ($2.0 \times 10^4$); **2Cr**$^{+}$ ($1.0 \times 10^6$); **2Pd**$^{+}$ ($1.8 \times 10^3$); **2Pt**$^{+}$ ($4.1 \times 10^3$). As the $K_c$ values exhibit the stabilities of the oxidized species, the chromium complex stabilizes the oxidized species, while palladium and platinum complexes destabilize the oxidized species (i.e., **2Pd**$^{+}$ is less stable than **2Cr**$^{+}$, for example).

This tendency is explainable also by effects of the metal center: one-electron oxidation of the ferrocenyl group generates a cation, in which positive charge delocalizes into the cyclobutene ring. In the case of **2Cr**$^{+}$, delocalization of the positive charge extends onto the chromium(0) metal and the system is stabilized by the contribution of Cr(I). On the other hand, in the case of palladium and platinum complex cations **2Pd**$^{+}$ and **2Pt**$^{+}$, the delocalization of positive charge extends onto the formal $M^{2+}$ metal, which has already been oxidized due to Lewis acidity. This delocalization leads to destabilization of the oxidized species. These phenomena are consistent with UV−vis spectral data mentioned above, which suggest charge delocalization onto the planar DPCB moiety.

## Conclusion

In conclusion, several noteworthy features have been found in this study: (1) the DPCB skeleton was applied as a linker of metal centers for the first time, and strong interactions between the iron centers via electronic delocalization to the cyclobutene ring was indicated. (2) Chelation of a transition metal affected the interactions between the iron centers in the oxidation process. Further studies of ferrocenyl and other metallocenyl group substituted DPCB derivatives and the mixed valence state of **1**$^{+}$ are underway in our laboratory.

## Experimental Section

**General Considerations.** Melting points were measured on a Yanagimoto MP-J3 micro melting point apparatus and are uncorrected. NMR spectra were recorded on a Bruker AVANCE-400 or a Bruker AM-600 spectrometer. IR spectra were obtained on a Horiba FT-300 spectrometer. MS data were taken on either a JEOL HX-110 or a Hitachi M-2500S spectrometer. Cyclic voltammograms were recorded on a BAS-CV-50W voltammetric analyzer under nitrogen. Elemental analyses were performed at Instrumental Analysis Center for Chemistry, Graduate School of Science, Tohoku University. Reactions were performed under an argon atmosphere, unless otherwise specified. Starting materials except for $Mes^*PH_2$ were obtained from commercial suppliers and used without purification.

**Preparation of 1,2-Diferrocenyl-3,4-diphosphinidenecyclobutene (1).** A mixture of (2,4,6-tri-*tert*-butylphenyl)phosphine (486.6 mg, 1.748 mmol) and 2,2′-azobisisobutyronitrile (AIBN) (17.2 mg, 0.105 mmol) in carbon tetrachloride (5.3 mL) was refluxed for 4 h and concentrated. THF (4.0 mL) was added to the residual material, chloro(2,4,6-tri-*tert*-butylphenyl)phosphine. To a solution of **3** (629.0 mg, 1.748 mmol) in THF (4.0 mL) was added 3.50 mol of $n$-butyllithium (1.59 M solution in hexane) at −78 °C. The resulting solution was stirred for 1 h and allowed to warm to room temperature. After the solution was stirred for 1 h, it was added to a THF solution of the chlorophosphine at room temperature. The mixture was stirred for 1 h, concentrated, and purified by silica gel column chromatography to give 505.5 mg (1.039 mmol, 60% yield) of **4**. To a solution of **4** (71.3 mg, 0.147 mmol) in THF (0.50 mL) was added 0.150 mmol of $n$-butyllithium (1.58 M solution in

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(14) Although the CV of the $Cr(CO)_4$ complex of 3,4-bis(2,4,6-tri-*tert*-butylphenyl)phosphinidene-1,2-bis(trimethylsilyl)cyclobutene[9a] exhibited only one reversible oxidation wave at 0.53 V under similar conditions, the second oxidation potential of **2Cr** (0.56 V) seems to correspond to the ferrocenyl oxidation, because the third potential (0.97 V, irreversible) is too large as a ferrocenyl oxidation wave.

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hexane) at −78 °C. The reaction mixture was stirred for 10 min, treated with 1,2-dibromoethane (0.0696 mmol) at −78 °C, and stirred for 10 min. The resulting mixture was then allowed to warm to room temperature and stirred for 1 h. The volatile materials were removed under reduced pressure. Toluene (0.5 mL) was then added to the residue. The mixture was refluxed for 30 min, concentrated, and purified by silica gel column chromatography to give 45.8 mg (0.0472 mmol, 64% yield) of **1**. Purple solid (melting point was unclear because it gradually decomposed above 100 °C): $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 1.45 (18H, s, Me), 1.63 (36H, br, Me), 4.00 (10H, s, ferrocene), 4.09 (4H, br, ferrocene), 4.24 (4H, br, ferrocene), 7.48 (4H, br, *m*-arom.); $^{13}$C{$^1$H } NMR (100 MHz, $CDCl_3$) $\delta$ 32.0 (s, Me), 33.6 (br, Me), 35.5 (s, *C*Me$_3$), 38.7 (s, *C*Me$_3$), 69.9 (s, ferrocene), 122.3 (br, *m*-Mes*), 137.0 (pseudo t, *ipso*-Mes*, $J_{PC}$ = 27.4 Hz), 150.5 (s, *p*-Mes*), 154.7 (pseudo t, P=C−*C*, $J_{PC}$ = 4.3 Hz), 155.6 (br, *o*-Mes*), 177.3 (dd, P=C, $J_{PC}$ = 18.1, 10.2 Hz); $^{31}$P{$^1$H} NMR (162 MHz, $CDCl_3$) $\delta$ 154.2; IR (KBr) $\nu$/cm$^{-1}$ 2959, 2904, 2879, 1473, 1257, 1101, 1024, 814; UV−vis (hexane) 344 (log $\epsilon$ 4.36), 523 nm (3.52); HRMS (70 eV, EI) found *m/z* 970.4131, calcd for $C_{60}H_{76}Fe_2P_2$ 970.4116. Anal. Calcd for $C_{61}H_{78}Fe_2P_2Cl_2$ (**1** + $CH_2Cl_2$): C, 69.39; H, 7.45. Found: C, 69.20; H, 7.49.

**Preparation of 1,2-Diferrocenyl-3,4-diphosphinidenecyclobutene−Transition Metal Complexes (2). 2Cr.** A mixture of **1** (61.5 mg, 0.0634 mmol) and (norbornadiene)Cr(CO)$_4$ (33.0 mg, 0.129 mmol) was dissolved in THF (2.0 mL) and was stirred at room temperature until disappearance of the starting DPCB (by TLC) was observed. The residue was purified by column chromatography (elution with hexane/ethyl acetate mixtures) to give **2Cr** almost quantitatively. Black solid (melting point was unclear because it gradually decomposed above 100 °C): $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 1.47 (18H, s, Me), 1.71 (36H, s, Me), 4.00 (10H, s, ferrocene), 4.16 (4H, s, ferrocene), 7.60 (4H, d, *m*-arom.); $^{13}$C{$^1$H } NMR (150 MHz, $CDCl_3$) $\delta$ 31.5 (s, Me), 33.9 (s, Me), 35.3 (s, *C*Me$_3$), 38.8 (s, *C*Me$_3$), 68.9 (br, ferrocene), 69.6 (s, ferrocene), 70.2 (s, ferrocene), 74.3 (s, ferrocene), 122.4 (s, *m*-Mes*), 130.7 (d, *ipso*-Mes*, $J_{PC}$ = 6.0 Hz), 152.3 (s, *p*-Mes*), 153.0 (dd, P=C−*C*, $J_{PC}$ = 54.3, 34.7 Hz), 157.8 (s, *o*-Mes*), 177.6 (dd, P=C, $J_{PC}$ = 30.2, 22.6 Hz), 219.9 (t, CO, $J_{PC}$ = 18.1 Hz), 228.2 (d, CO, $J_{PC}$ = 6.0 Hz); $^{31}$P{$^1$H } NMR (162 MHz, $CDCl_3$) $\delta$ 170.0 (br); IR (KBr) $\nu$ /cm$^{-1}$ 2962, 2910, 2871, 2011, 1919, 1886, 1587, 1473, 1398, 1252, 819, 671, 633, 482; UV−vis ($CH_2Cl_2$) 329 (log $\epsilon$ 4.46), 456 nm (4.23); HRMS (70 eV, EI) found *m/z* 1022.3533, calcd for $C_{60}H_{76}CrFe_2P_2$ [M$^+$ − 4CO] 1022.3520.

**2Mo.** A mixture of **1** (11.0 mg, 0.0113 mmol) and (norbornadiene)Mo(CO)$_4$ (5.1 mg, 0.017 mmol) was dissolved in THF (0.5 mL) and was stirred at room temperature until disappearance of the starting DPCB was observed by TLC. The residue was purified by column chromatography (elution with hexane/ethyl acetate mixtures) to give **2Mo** almost quantitatively. Black solid (melting point was unclear because it gradually decomposed above 100 °C): $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 1.47 (18H, s, Me), 1.72 (36H, s, Me), 4.01 (10H, s, ferrocene), 4.17 (6H, s, ferrocene), 7.60 (4H, d, *m*-arom.); $^{13}$C{$^1$H} NMR (150 MHz, $CDCl_3$) $\delta$ 31.5 (s, Me), 34.0 (s, Me), 35.3 (s, *C*Me$_3$), 38.9 (s, *C*Me$_3$), 69.1 (s, ferrocene), 69.6 (s, ferrocene), 70.3 (s, ferrocene), 74.2 (s, ferrocene), 122.5 (s, *m*-Mes*), 130.4 (s, *ipso*-Mes*), 152.3 (s, *p*-Mes*), 153.3 (dd, P=C−*C*, $J_{PC}$ = 54.3, 33.2 Hz), 157.5 (s, *o*-Mes*), 177.8 (dd, P=C, $J_{PC}$ = 27.2, 22.4 Hz), 209.3 (t, CO, $J_{PC}$ = 12.1 Hz), 217.1 (dd, CO, $J_{PC}$ = 37.7, 7.5 Hz); $^{31}$P{$^1$H} NMR (162 MHz, $CDCl_3$) $\delta$ 153.4; IR (KBr) $\nu$ /cm$^{-1}$ 2962, 2021, 1921, 1886, 1261, 1097, 1026, 806; UV−vis ($CH_2Cl_2$) 328 (log $\epsilon$ 4.31), 430 (4.19), 532 nm (3.80); HRMS (70 eV, EI) found *m/z* 1068.3225, calcd for $C_{60}H_{76}Fe_2MoP_2$ [M$^+$ − 4CO] 1068.3204.

**2W.** A mixture of **1** (87.4 mg, 0.0900 mmol) and (norbornadiene)W(CO)$_4$ (69.9 mg, 0.180 mmol) was dissolved in THF (2.0 mL) and was stirred at 50 °C. The residue was purified by column chromatography (elution with hexane/ethyl acetate mixtures) to give **2W** (82.3 mg, 0.650 mmol, 72% yield). Black solid (melting point was unclear because it gradually decomposed above 100 °C): $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 1.48 (18H, s, Me), 1.72 (36H, s, Me), 4.01 (10H, s, ferrocene), 4.18 (4H, s, ferrocene), 7.61 (4H, d, *m*-arom.); $^{13}$C{$^1$H} NMR (150 MHz, $CDCl_3$) $\delta$ 31.5 (s, Me), 34.1 (s, Me), 35.3 (s, *C*Me$_3$), 39.0 (s, *C*Me$_3$), 69.0 (br, ferrocene), 69.6 (s, ferrocene), 70.4 (s, ferrocene), 74.0 (s, ferrocene), 122.6 (s, *m*-Mes*), 129.4 (s, *ipso*-Mes*), 152.1 (dd, P=C−*C*, $J_{PC}$ = 57.3, 34.7 Hz), 152.5 (s, *p*-Mes*), 157.8 (s, *o*-Mes*), 180.1 (dd, P=C, $J_{PC}$ = 36.2, 22.6 Hz), 203.5 (t, CO, $J_{PC}$ = 10.6 Hz), 207.4 (m, CO); $^{31}$P{$^1$H} NMR (162 MHz, $CDCl_3$) $\delta$ 132.9 (satellite, $^1J_{PW}$ = 256.6 Hz); IR (KBr) $\nu$/cm$^{-1}$ 2960, 2870, 2017, 1913, 1886, 1585, 1471, 1398, 1363, 1261, 1105, 1007, 881, 818, 629, 596, 499, 455; UV−vis ($CH_2Cl_2$) 328 (log $\epsilon$ 4.46), 431 (4.37), 543 nm (3.99); HRMS (70 eV, EI) found *m/z* 1154.3627, calcd for $C_{60}H_{76}Fe_2P_2W$ [M$^+$ − 4CO] 1154.3649.

**2Pd.** A mixture of **1** (10.7 mg, 0.0110 mmol) and Pd(MeCN)$_2$Cl$_2$ (3.0 mg, 0.0116 mmol) was dissolved in THF (0.5 mL) and was stirred at room temperature until TLC-observed disappearance of the starting DPCB. The residue was purified by column chromatography (elution with hexane/ethyl acetate mixtures) to give **2Pd** almost quantitatively. Black solid (melting point was unclear because it gradually decomposed above 100 °C): $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 1.41 (18H, s, Me), 1.74 (36H, s, Me), 3.73 (4H, s, ferrocene), 4.06 (10H, s, ferrocene), 4.33 (4H, s, ferrocene), 7.62 (4H, s, *m*-arom.); $^{13}$C{$^1$H} NMR (150 MHz, $CDCl_3$) $\delta$ 31.3 (s, Me), 34.8 (br, Me), 35.5 (s, *C*Me$_3$), 39.5 (s, *C*Me$_3$), 68.0 (s, ferrocene), 69.4 (s, ferrocene), 70.2 (s, ferrocene), 71.9 (s, ferrocene), 72.7 (s, ferrocene), 122.3 (t, *ipso*-Mes*, $J_{PC}$ = 7.5 Hz), 123.8 (t, *m*-Mes*, $J_{PC}$ = 4.5 Hz), 152.3 (m, P=C−*C*), 155.0 (s, *p*-Mes*), 157.4 (s, *o*-Mes*), 166.3 (dd, P=C, $J_{PC}$ = 49.8, 39.2 Hz); $^{31}$P{$^1$H} NMR (162 MHz, $CDCl_3$) $\delta$ 134.9; IR (KBr) $\nu$/cm$^{-1}$ 2954, 2923, 2906, 1591, 1475, 1267, 821, 644, 459; UV−vis ($CH_2Cl_2$) 315 (log $\epsilon$ 4.46), 370 (4.58), 573 nm (3.84); HRMS (70 eV, EI) found *m/z* 1076.3190, calcd for $C_{60}H_{76}Fe_2P_2Pd$ [M$^+$ − 2Cl] 1076.3183.

**2Pt.** A mixture of **1** (11.0 mg, 0.0133 mmol) and Pt(PhCN)$_2$Cl$_2$ (10.0 mg, 0.0212 mmol) was dissolved in THF (1.0 mL) and was stirred at 50 °C. The residue was purified by column chromatography (elution with hexane/ethyl acetate mixtures) to give **2Pt** (8.6 mg, 0.070 mmol, 52% yield). Black solid (melting point was unclear because it gradually decomposed above 100 °C): $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 1.41 (18H, s, Me), 1.76 (36H, s, Me), 3.87 (4H, br, ferrocene), 4.05 (10H, s, ferrocene), 4.28 (4H, s, ferrocene), 7.65 (4H, d, *m*-arom.); $^{13}$C{$^1$H} NMR (150 MHz, $CDCl_3$) $\delta$ 31.2 (s, Me), 34.6 (s, Me), 35.4 (s, *C*Me$_3$), 39.5 (s, *C*Me$_3$), 69.0 (s, ferrocene), 69.9 (s, ferrocene), 71.3 (s, ferrocene), 73.0 (s, ferrocene), 119.8 (d, *ipso*-Mes*, $J_{PC}$ = 33.2 Hz), 123.8 (pseudo t, *m*-Mes*), 150.5 (dd, P=C−*C*, $J_{PC}$ = 60.4, 30.2 Hz), 154.8 (s, *p*-Mes*), 157.8 (s, *o*-Mes*), 163.9 (dd, P=C, $J_{PC}$ = 81.5, 16.6 Hz); $^{31}$P{$^1$H} NMR (162 MHz, $CDCl_3$) $\delta$ 111.4 (satellite, $^1J_{PPt}$ = 4486.0 Hz); IR (KBr) $\nu$/cm$^{-1}$ 2962, 1593, 1475, 1265, 1099, 1053, 1026, 816, 646, 461; UV−vis ($CH_2Cl_2$) 264 (log $\epsilon$ 4.53), 379 (4.43), 556 nm (3.93); HRMS (70 eV, EI) found *m/z* 1063.3635, calcd for $C_{60}H_{74}Fe_2P_2Pt$ [M$^+$ − 2H − 2Cl] 1163.3623.

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**Supporting Information Available:** $^1$H NMR spectra of **1** and **2** at 600 MHz at room temperature and variable-temperature $^1$H NMR spectra of **1** and **2Pd**. This material is available free of charge via the Internet at http://pubs.acs.org.

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