Preparation and Properties of 1,2-Bis[(2,4,6-tri-*t*-butylphenyl)phosphinidene]cyclobuta[*l*]phenanthrene

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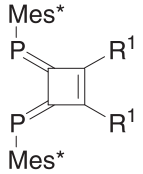
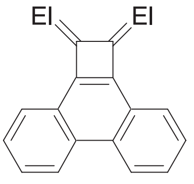
Sterically protected 1,2-bis[(2,4,6-tri-*t*-butylphenyl)phosphinidene]cyclobuta[*l*]phenanthrene (**4**) and its group(6) and group(10) transition metal complexes were prepared. X-ray crystallographic analysis of **4** revealed a planar structure of the diphosphinidenecyclobuta[*l*]phenanthrene moiety.

Sterically protected 3,4-diphosphinidenecyclobutenes (**1**: abbreviated to DPCB),[1] bearing an extremely bulky 2,4,6-tri-*t*-butylphenyl group (abbreviated as Mes*)[2] are unique ligands of interest,[3] because of their relatively rigid framework containing phosphorus–carbon π-bonds,[4] whose low-lying π^* orbital[3d] plays an important role in catalytic activity of their transition metal complexes.[3b–e]

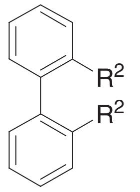
DPCB derivatives containing phenyl groups at the 1,2-positions, such as **1b**, **1c** have been reported.[1a,3c] X-ray crystallographic data from (*E*,*E*)-**1b** suggest that the aromatic rings at the 1,2-positions are not co-planar, at least in the crystalline state.[1a] Extension of the π-system of the DPCB moiety with a planar aromatic skeleton is of interest, because the extended π-conjugation may affect the frontier orbitals, which in turn affect electronic states and catalytic activity.[3d]



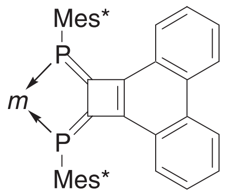
(*E*,*E*)-**1a**: R^1 = H
(*E*,*E*)-**1b**: R^1 = Ph
(*E*,*E*)-**1c**: R^1 = *p*-MeOC$_6$H$_4$



2: El = O; **3**: El = S



5: R^2 = CHO
6: R^2 = CH=CBr$_2$
7: R^2 = C≡CP(H)Mes*



(*E*,*E*)-**4**: *m* = none
9Cr: *m* = Cr(CO)$_4$
9Mo: *m* = Mo(CO)$_4$
9W: *m* = W(CO)$_4$
9Pd: *m* = PdCl$_2$
9Pt: *m* = PtCl$_2$

Mes* = 2,4,6-*t*-Bu$_3$C$_6$H$_2$

Extension of the π-system by incorporation of a planar fused-ring aromatic system such as phenanthrene is thus of interest. We report here the preparation and properties of diphosphinidenecyclobuta[*l*]phenanthrene **4** as well as its transition metal complexes. It should be noted here that cyclobuta[*l*]phenanthrene derivatives such as **2** or **3** have rarely been studied,[5] in contrast to the abundant research on phenanthrene derivatives.

Compound **4** was prepared by an ordinary method[1b] as follows. Bis-olefination of **5**[6] with a CBr$_4$/PPh$_3$ derived ylide[7] provided **6**. Treatment of **6** with *n*-BuLi followed by Mes*PHCl[8] gave **7**. Compound **7** was then treated with *n*-BuLi (2 molar ratio) and 1,2-dibromoethane (1 molar ratio) in a dilute THF solution to give **4** [(*E*,*E*)-form] in 10% yield.[9]

The structure of (*E*,*E*)-**4** was unambiguously determined by X-ray crystallography.[10] Figure 1 shows a molecular structure of (*E*,*E*)-**4**, which has a C_2 symmetry. The cyclobutaphenanthrene moiety was almost planar [deviation of atoms C(1)–C(8) and C(1)*–C(8)* from planarity was within 0.03(1) Å]. Table 1 lists selected bond lengths of (*E*,*E*)-**4** as well as those of the related compounds (*E*,*E*)-**1b**,[1a] **2**,[5a] and parent phenanthrene (**8**).[11] The P(1)–C(1), P(1)–C(9), and C(1)–C(1)* bond lengths of **4** are slightly shorter than those of **1b**, while C(1)–C(2) is longer in **4** than in **1b**. The bond lengths in the phenanthrene moiety of **4** are in general very similar to those of **2** and **8**. The C(1)–C(1)* bond length for **2**, however, is apparently longer than that for **4**: this may be due to the electrostatic repulsion between the two carbonyl groups. The difference between the bond lengths of **4** and **1b** mentioned above suggests that the phenanthrene system co-planar to the –P=C–C=P– moiety affect the P=C π-bond.

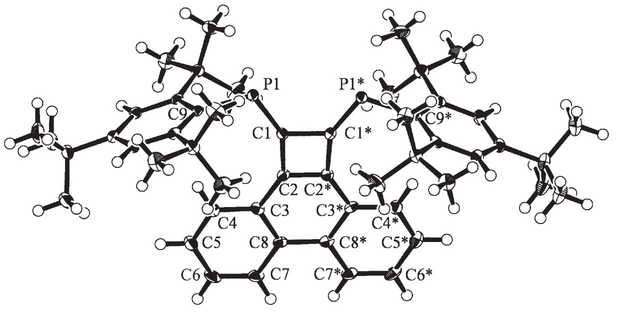


Figure 1. Molecular structure of (*E*,*E*)-**4**, showing the atomic labeling scheme with thermal ellipsoids (50% probability).

UV–vis spectra of compounds **1a**,[1c] **1b**,[1a] and **4** are shown in Figure 2. The absorption of **4** at 260–300 seems to be due to phenanthrene ring system. Preliminary calculation (HF/3-21G) of a model (*p*-*t*-Bu was replaced by H) of (*E*,*E*)-**4** indicated that HOMO is π-orbital (rather than n orbital) containing P=C and phenanthrene π-system, and energy gap between LUMO and LUMO+1 is smaller than that of the corresponding 1,2-diphenyl derivative. The absorption of **4** at 340–400 nm appears to correspond to the $\pi \rightarrow \pi^*$ transitions.

^{31}P NMR spectrum of (*E*,*E*)-**4** [δ_P (CDCl$_3$) 173.8] shows a shift to a lower field, compared with that for (*E*,*E*)-**1b** [δ_P (CDCl$_3$) 169.7]. Although chemical shift of the α-carbon (C1 in Figure 1) of (*E*,*E*)-**4** is similar to that of (*E*,*E*)-**1b** in ^{13}C NMR spectrum, the β-carbon (C2) shifts to a higher field in (*E*,*E*)-**4** [(*E*,*E*)-**4**: δ(C1) 177.8, δ(C2) 149.6; (*E*,*E*)-**1b**[1a]: δ(C1) 176.3, δ(C2) 155.3].

Table 1. Selected bond lengths (Å) for compounds (*E*,*E*)-**1b**, (*E*,*E*)-**4**, **2**, and **8**

	(*E*,*E*)-**4**	(*E*,*E*)-**1b**[a]	**2**[b]	**8**[c]
P(1)–C(1)	1.669(2)	1.690(8)	—	—
P(1)–C(9)	1.841(1)	1.861(6)	—	—
C(1)–C(2)	1.488(2)	1.467(10)	1.489[d]	—
C(2)–C(3)	1.430(2)	—	1.423[d]	1.422[d]
C(1)–C(1)*	1.515(6)	1.535(8)	1.580	—
C(2)–C(2)*	1.380(2)	1.380(9)	1.362	1.338

[a] Data taken from Ref. 1a. [b] Data taken from Ref. 5a. [c] Data taken from Ref. 11. [d] Taking approximate C_{2v} symmetry of the molecule into account, the corresponding two bond lengths are averaged.

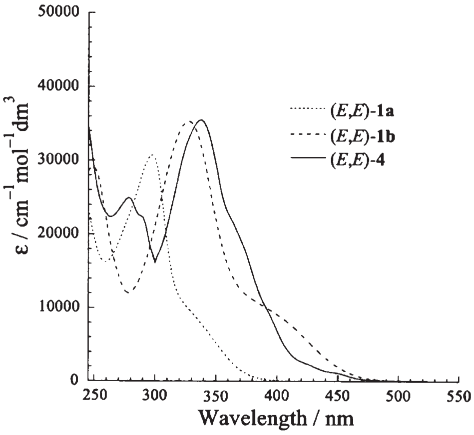


Figure 2. UV–vis spectra of (*E*,*E*)-**1a**, (*E*,*E*)-**1b**, and (*E*,*E*)-**4** in CH_2Cl_2.

We then prepared several transition metal complexes of **4** as follows. Reaction of (*E*,*E*)-**4** with [group(6) transition metal]-[(bicyclo[2.2.1]hepta-2,5-diene)tetracarbonyl] gave the corresponding chelate tetracarbonylmetal complexes **9Cr**,**Mo**,**W**.[12] When (*E*,*E*)-**4** was treated with $(RCN)_2MCl_2$ [(M = Pd, R = Me) or (M = Pt, R = Ph)], chelate complexes **9Pd**,**Pt** were formed.[12] Although the $^1J_{WP}$ of **9W** is similar to that of (*E*,*E*)-**1b**•$W(CO)_4$ complex ($^1J_{WP} = 257$ Hz), the $^1J_{PtP}$ of **9Pt** is apparently smaller than that of (*E*,*E*)-**1b**•$PtCl_2$ complex ($^1J_{PtP} = 4499.2$ Hz). The reason for this small $^1J_{PtP}$ value in **9Pt** is not clear at this time. The structure-J_{PtP} relationship is still unclear in other known DPCB•$PtCl_2$ complexes.

In summary, we have prepared diphosphinidenecyclobuta[*l*]phenanthrene derivative for the first time. A planar structure was confirmed by X-ray crystallography. Electronic perturbation was shown by UV–vis and NMR spectroscopies. Further studies on the properties of **4** and **9** are now in progress.

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9 (*E*,*E*)-**4**: Yellow solid, mp >275 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1.53$ (18H, *p*-*t*-Bu), 1.59 (36H, *o*-*t*-Bu), 5.64 (2H, d, $^3J_{HH} = 8.0$ Hz, arom.), 7.00 (2H, t, $^3J_{HH} = 7.6$ Hz, arom.), 7.43 (2H, t, $^3J_{HH} = 7.4$ Hz, arom.), 7.65 (4H, *m*-Mes*), and 8.47 (2H, d, $^3J_{HH} = 8.4$ Hz, arom.); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta = 32.1$ (*p*-C*Me*$_3$), 33.6 (*o*-C*Me*$_3$), 35.7 (*p*-*C*Me$_3$), 38.9 (*p*-*C*Me$_3$), 122.5 (*m*-Mes*), 123.6, 125.7, 127.3, 127.5, 127.9, 132.3, 136.6 (pseudo t, $J_{PC} = 18.1$ Hz, *ipso*-Mes*), 149.6 (pseudo t, $J_{PC} = 4.0$ Hz, P=C–*C*), 151.2, 156.5, and 177.8 (dd, $^1J_{PC} = 16.5$ Hz and $^3J_{PC} = 7.0$ Hz, P=C); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) $\delta = 173.8$; IR (KBr) 2960, 2908, 2870, 1593, 1473, 1396, 1362, 1238, 1209, and 758 cm^{-1}; UV–vis (hexane) 278 (log ε 4.40), 290 (sh, 4.35), and 338 nm (4.55). Found: m/z 753.4711. Calcd. for $C_{52}H_{67}P_2$, MH^+, 753.4713.

10 $C_{52}H_{66}P_2$, $M_r = 753.04$. monoclinic, space group C2 (#5), $a = 14.948(5)$, $b = 10.385(3)$, $c = 15.264(6)$ Å, $\beta = 106.963(2)°$, $V = 2266.3(14)$ Å^3, $Z = 2$, $\rho = 1.103$ gcm^{-3}, $\mu = 1.29$ cm^{-1}; R_1 $[I > 2\sigma(I)] = 0.034$, R = 0.036 (all data), wR_2 (all data) = 0.076. 5171 Unique reflections with $2\theta \leq 55.0°$ were recorded (Mo Kα radiation, graphite monochrometer) at −100 °C. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (No. CCDC 241967).

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12 **9Cr**: Brown solid, mp 165–168 °C (decomp.); ^{31}P NMR (162 MHz, $CDCl_3$) $\delta = 193.1$; UV–vis (CH_2Cl_2) 247 (log ε 4.85), 339 (4.46), and 456 nm (4.29). **9Mo**: Brown solid, mp > 160 °C (decomp.); ^{31}P NMR $\delta = 176.3$; UV–vis (CH_2Cl_2) 245 (log ε 4.92), 334 (4.50), and 436 nm (4.42). **9W**: Brown solid, mp 222–226 °C (decomp.); ^{31}P NMR $\delta = 154.4$ (satellite d, $^1J_{WP} = 256.4$ Hz); UV–vis (CH_2Cl_2) 244 (log ε 4.95), 334 (4.52), 437 (4.52), and 530 nm (3.88). **9Pd**: Brown solid, mp 231–234 °C (decomp.); ^{31}P NMR $\delta = 149.5$; UV–vis (CH_2Cl_2) 249 (log ε 4.73) and 359 nm (4.63). **9Pt**: Orange solid, mp > 300 °C (decomp.); ^{31}P NMR $\delta = 125.7$ (satellite d, $^1J_{PtP} = 4441.4$ Hz); UV–vis (CH_2Cl_2) 250 (log ε 4.62), 261 (4.60), 274 (4.61), and 365 nm (4.67).

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