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PAPER

Different coordination modes of 2-(diphenylphosphino)azobenzenes in complexation with hard and soft metals[†]

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Control of coordination modes of a ligand in metal complexes is significant because the coordination modes influence catalytic properties of transition metal catalysts. Reactions of 2-diphenyl-phosphinoazobenzenes, which are in equilibrium with the inner phosphonium salts, with ZnCl₂, W(CO)₅(THF), and PtCl₂(cod) gave three different coordination types of metal complexes with distinctive UV-vis absorptions. All the complexes were characterized by X-ray crystallographic analyses. In the zinc and tungsten complexes, the source molecule functions as an amide ligand and a phosphine ligand, respectively. In the platinum complex, the phosphorus molecule works as a tridentate ligand with formation of a carbon–platinum bond.

Introduction

Both phosphines and amides have been widely used as ligands for transition metal complexes.¹ Their coordination modes are so different that the choice of the ligands can influence metalcatalyzed reactions. There are few examples for reversible conversion between trivalent-tricoordinated and pentavalenttetracoordinated organophosphorus compounds because most nucleophilic displacement reactions of trivalent phosphines with electrophiles are irreversible. In the continuation of our study on phosphorus compounds bearing an azobenzene moiety,² we previously reported the synthesis of diphenyl[2-(phenylazo)phenyl]phosphines ((E)-1a,b) and its equilibrium with the corresponding inner phosphonium salts 2a,b, which possessed a bond between the phosphorus and the nitrogen atoms in the solution state (Scheme 1).^{3,4} The equilibrium ratio was influenced by various factors, such as temperature, solvent, additives, and light. Phosphine (E)-1a was expected to act as an ambidentate ligand for metal complexes. We report here reactions of the phosphines containing an azobenzene moiety with some metal sources to give the corresponding phosphine complexes or amide complexes.

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 $(CO)_5$ and (E)-**3b**, respectively. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt31494k

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Scheme 1 An equilibrium between phosphines (*E*)-1 and inner phosphonium salts 2, and its complexation giving $2a \cdot \text{ZnCl}_2 \cdot (\text{THF})$.

Results and discussion

Amide complex

The dark red colored equilibrium mixture of (*E*)-1a and the corresponding inner phosphonium salt 2a was treated with zinc dichloride in THF at room temperature. The resulting THF solution showed only one broad singlet at δ 42.7 in the ³¹P NMR spectrum, which was assigned to a phosphonium salt, indicating quantitative formation of the corresponding zinc–amide complex 2a·ZnCl₂·(THF). The complex was isolated in 90% yield (Scheme 1). A reaction of (*E*)-1b with ZnCl₂ in THF gave a result similar to the reaction of (*E*)-1a. The zinc complex, similar to 2a, is very sensitive to humidity.

A reaction of (*E*)-1a with $\text{LiB}(\text{C}_6\text{F}_5)_4$ in THF induced color change of the solution to colorless and low field shift (δ 38.6) in the ³¹P NMR spectrum. Although formation of the lithium– amide complex was indicated by these results, isolation of the complex was not successful.

The crystal structure of $2a \cdot ZnCl_2 \cdot (THF)$ was determined by X-ray crystallographic analysis (Fig. 1, Table 1). The P1 atom has a tetrahedral structure and Zn1 atom is coordinated by both 2a through the N1 atom and one THF molecule through the O1

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Fig. 1 ORTEP drawing of $2a \cdot 2n \operatorname{Cl}_2$ (THF) with thermal ellipsoid (50% probability). A free THF molecule was omitted for clarity. Selected bond lengths (Å) and angles (°): P1–N2, 1.679(3); P1–C1, 1.739(3); P1–C13, 1.775(3); P1–C19, 1.797(3); N1–N2, 1.445(4); N1–Zn1, 2.0012(2); Cl1–Zn1, 2.2383(10); Cl2–Zn1, 2.2315(10); O1–Zn1, 2.048(2); N2–P1–C1, 93.50(14); N2–P1–C13, 111.56(14); N2–P1–C19, 110.58(15); C1–P1–C13, 115.66(15); C1–P1–C19, 116.63(15); C13–P1–C19, 108.18(15); P1–N2–N1, 112.42(19); P1–N2–C7, 117.8(2); N2–N1–C6, 108.3(2); N2–N1–Zn1, 113.61(18); C6–N1–Zn1, 119.15(17); N1–Zn1–Cl1, 109.96(9); N1–Zn1–Cl2, 108.57(9); N1–Zn1–O1, 107.50(9); Cl1–Zn1–Cl2, 126.53(3); Cl1–Zn1–O1, 100.70(8); Cl2–Zn1–O1, 101.48(7).

Table 1 Crystallographic data

Complex	$2a \cdot ZnCl_2 \cdot (THF)$	$(E)-\mathbf{1b}\cdot W(CO)_5$	(E)- 3b
Formula Formula	C ₂₈ H ₂₇ Cl ₂ N ₂ OPZn 574.46	$\begin{array}{c} C_{31}H_{23}N_2O_5PW \\ 718.33 \end{array}$	C ₂₆ H ₂₂ ClN ₂ PPt 623.97
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_{1}2_{1}2_{1}$	$P2_{1}/c$	$P2_1/n$
a(Å)	9.3362(15)	9.5272(18)	8.632(4)
b(Å)	16.298(3)	21.273(2)	17.191(8)
c(Å)	17.254(3)	14.448(2)	15.216(7)
$\beta(\circ)$	_	104.319(3)	96.028(2)
$V(Å^3)$	2625.4(7)	2837.3(8)	2245.5(18)
Z	4	4	4
$D_{\rm c} ({\rm Mg} {\rm m}^{-3})$	1.454	1.682	1.846
$T(\mathbf{K})$	133	120	120
Measured reflections	20 723	17 582	14 108
Unique reflections	5950	4979	3887
Rint	0.0345	0.0216	0.0222
$R_1^{\text{IIII}}(I > 2\sigma(I))$	0.0303	0.0209	0.0193
wR_2 (all data)	0.0908	0.0508	0.0477
GOF	1.104	1.089	1.079

atom. The N1–N2 (1.445(4) Å) bond length falls within the range of usually observed N–N single bond lengths. The bond angles around the P1 atom are between 93.50(14)–116.63(15)°. The P1–N2 bond length (1.679(3) Å) and the P1–C bond lengths (1.739(3)–1.797(3) Å), the latter of which are much



Scheme 2 Formation of complexes, (E)-1b·W(CO)₅ and (E)-3b.

shorter than those of 2-diphenylphosphinoazobenzene,³ are almost the same as the corresponding bond lengths of (N',N'-dimethylhydrazino)triphenylphosphonium bromide (P–N: 1.640(3) Å; P–C: 1.776(3)–1.787(3) Å).⁵ These structural features clearly indicate the existence of the P–N bond and hydrazinophosphonium structure around the phosphorus moiety in the zinc complex. The sum of the bond angles around the N1 and N2 atoms (341.1° and 348.0°, respectively) revealed a considerable pyramidalization.

Phosphine complex

Reaction of (*E*)-**1b** with W(CO)₅(THF) gave tungsten–phosphine complex (*E*)-**1b**·W(CO)₅ (δ_P 19.1 (s, ${}^1J_{W-P} = 246$ Hz)) in 75% yield (Scheme 2). The formation of the phosphine complex as a stable form in the air is in marked contrast to the formation of the amide complex in the reaction of zinc chloride. The crystal structure of (*E*)-**1b**·W(CO)₅ was determined by X-ray crystallographic analysis (Fig. 2, Table 1). The structure around the P1 and W1 atoms is quite normal for a phosphine–tungsten complex and there is no interaction between P1 and the azo moiety. Although there has been a report of the synthesis of similar phosphine complexes, 2-(PhN=N)C₆H₄P(R)(OH)W-(CO)₅ via a phosphinidene complex, RPW(CO)₅, where the R is Ph or Me,⁶ the present synthetic method using the phosphine is more straightforward and rational.



Fig. 2 ORTEP drawing of (*E*)-**1b**·W(CO)₅ (50% probability). Selected bond lengths (Å) and angles (°) of (*E*)-**1b**·W(CO)₅: P1–C1, 1.846(3); P1–C15, 1.832(3); P1–C21, 1.843(3); N1–N2, 1.259(3); P1–W1, 2.5582(8); W1–C31, 2.039(3); C1–P1–C15, 105.43(12); C1–P1–C21, 102.35(13); C15–P1–C21, 100.61(12); W1–P1–C1, 120.00(9); W1–P1–C15, 113.29(9); W1–P1–C21, 112.90(9).



Fig. 3 ORTEP drawing of (*E*)-**3b** (50% probability). Selected bond lengths (Å) and angles (°) of (*E*)-**3b**: P1–C1, 1.824(3); P1–C15, 1.816(3); P1–C21, 1.814(3); N1–N2, 1.274(3); Pt1–P1, 2.29150(10); Pt1–N1, 1.972(3); Pt1–C12, 2.023(3); Pt1–C11, 2.3089(11); C1–P1–C15, 104.79(14); C1–P1–C21, 108.24(14); C15–P1–C21, 103.94(14); P1–Pt1–N1, 85.25(8); P1–Pt1–C12, 163.91(9); P1–Pt1–C11, 99.92(4); N1–Pt1–C12, 78.74(12); N1–Pt1–C11, 174.66(7); C12–Pt1–C11, 96.13(9).

Tridentate ligand complexes

Reaction of (E)-1b with PtCl₂(cod) gave tridentate complex (*E*)-**3b** (δ_P 30.2 (s, ${}^1J_{Pt-P} = 2072$ Hz)) together with another thermally unstable platinum complex (δ_P 1.2 (s, ${}^1J_{Pt-P} = 3566$ Hz)) bearing no Pt–C bond, and the latter complex turned into (E)-3b in solution. Finally, (E)-3b was obtained as a deep-red crystal in 66% yield. The Pt–P coupling constant of (E)-3b is considerably smaller than 3858 Hz (δ_P 8.2) of the previously reported complex, $[PtCl(C_6H_4-2-N=NPh-C,N)(PEt_3)]$,⁷ suggesting strong carbon-platinum bonding at the trans position of the phosphorus atom.⁸ The crystal structure of (E)-**3b** was determined by X-ray crystallographic analysis (Fig. 3, Table 1). The N-N bond length (1.274(3) Å), which is slightly longer than those of azobenzene and (E)-1b·W(CO)₅, is reasonable for a N=N double bond. The central platinum atom has a slightly distorted square planar structure. Generally, azobenzene reacts easily with a transition metal to give an ortho-metalated complex.9,10 After the first formation of an intermediary platinum complex coordinated by the phosphine and/or the azo moiety, intramolecular C-H insertion^{11,12} followed by reductive elimination via a high oxidation state of the platinum or σ -bond metathesis without the change of valence of the platinum would occur to give (E)-3b. The resulting complex (E)-3b is stable toward hydrolysis in contrast with (*E*)-2b and $2a \cdot ZnCl_2 \cdot (THF)$, probably because of no contribution of the phosphonium salt character by the complexation with zinc.

UV-vis spectroscopy

Colors of the solutions of the synthesized metal complexes depend on the coordination modes of the ligands. For example, $2\mathbf{a}\cdot \text{ZnCl}_2$ (THF) in THF was orange. The absorption maximum $(\lambda = ca. 420 \text{ nm})$ is quite shorter than that of (*E*)-1a ($\lambda =$ 473 nm) in THF. Since the difference of the absorption wavelengths are so large, the formation of $2\mathbf{a}\cdot \text{ZnCl}_2$ (THF) can be confirmed by monitoring of the UV-vis spectroscopy. In fact,



Fig. 4 UV-vis spectral change upon addition of zinc chloride to (*E*)-**1a** in THF.



Fig. 5 UV-vis spectra of (E)-1b·W(CO)₅, (E)-1b, and (E)-3b.

addition of zinc chloride to a THF solution of (E)-1a caused a decrease in the absorption maximum at 473 nm and an increase in a new absorption at 420 nm of $2a \cdot ZnCl_2 \cdot (THF)$ (Fig. 4). In contrast, addition of excess TMEDA to remove zinc chloride regenerated the dark red-colored (E)-1a (Fig. 4, Scheme 1).

The blue-shift in the absorption spectrum by complexation at nitrogen was also observed in the protonation of 2a.⁴ Since the dark red color of the phosphonium salt 2a was ascribed to several charge transfer excitations from the HOMO, which is the non-bonding orbital of the nitrogen atom at the high energy level, the coordination of the nitrogen to zinc lowered the energy level of the HOMO, which made the color of the zinc complex paler than 2a.

In the UV-vis spectra in dichloromethane, the absorptions of (E)-**1b**·W(CO)₅ (λ = 348 nm (log ε = 4.31)) and (E)-**3b** (λ = 490 nm (log ε = 3.70), 414 nm (4.23), 383 nm (4.20)) were observed at longer wavelengths than that of (E)-**1b** (λ = 335 nm (log ε = 4.32)) (Fig. 5). The red-shifts by metal complexation of (E)-**1b**, in contrast to the blue-shift observed in **2a**·ZnCl₂·(THF), are partly ascribed to absence of the phosphonium salt character.



Fig. 6 Selected molecular orbitals of (a) $2a \cdot \text{ZnCl}_2 \cdot (\text{THF})$ (left), (b) (*E*)-**1**b·W(CO)₅ (center), and (c) (*E*)-**3**b (right) calculated at the B3LYP functional with the basis sets 6-311+G(d,p) for C, H, N, O, P, and Cl, and LANL2DZ for Zn, W, and Pt.

To evaluate the effect of the complexation on the absorption property, single-point density functional theory (DFT) calculations and time-dependent DFT (TD-DFT) calculations were performed based on the crystal structures of $2a \cdot \text{ZnCl}_2$ (THF), (*E*)-1b·W(CO)₅ and (*E*)-3b at the B3LYP/LANL2DZ[Pt,Zn,W]/ 6-311+G(d,p)[C,H,N,O,P,Cl] level. The results are summarized in Fig. 6 and Table 2.

Firstly, in $2a \cdot ZnCl_2 \cdot (THF)$, the HOMO localizes on n_N orbitals conjugated with the π -orbital of the diarylhydrazine moiety, and the LUMO, LUMO+1 and LUMO+2 localize on the π^* orbital of the diphenylphosphino moiety. Such molecular orbitals are similar to the HOMO and LUMO of triphenyl[2-(2-phenylhydrazino)phenyl]phosphonium.⁴ The TD-DFT calculation of $2a \cdot ZnCl_2 \cdot (THF)$ indicates that transitions from the HOMO to unoccupied molecular orbitals around the positively charged phosphorus atom are responsible for the broad absorptions, and these transitions are considered to be charge transfer excitations.

Secondly, in (*E*)-**1**b·W(CO)₅, the HOMO, HOMO–1, and HOMO–2 consist of π orbitals of the diphenylphosphino moiety. The n and π orbitals of the azobenzene are found in the HOMO–3 and HOMO–4, respectively. The LUMO is representative of the π^* orbital of the azobenzene. The TD-DFT study suggests that the HOMO–3 \rightarrow LUMO and HOMO–4 \rightarrow LUMO transitions are n– π^* and π – π^* transitions of the azobenzene moiety, respectively. Reflecting their large oscillator

Table 2	Selected	calculated	singlet	excited	energies	for
2a·ZnCl ₂	\cdot (THF), (E) \cdot	-1 b ·W(CO) ₅ ,	and (\bar{E}) -3b			

		Transition	Excitation energy/nm	Oscillator strength	
2a ·ZnCl ₂ ·(THF)	S_1	HOMO → LUMO	554	0.0161	
,	S_2	$HOMO \rightarrow LUMO+1$	471	0.0081	
	S_3	HOMO \rightarrow LUMO+2	415	0.0067	
	S_4	HOMO \rightarrow LUMO+3	383	0.0216	
	S_5	$HOMO \rightarrow LUMO+4$	360	0.0405	
$(E)-\mathbf{1b}\cdot W(CO)_5$	S_1	$HOMO \rightarrow LUMO$	507	0.0022	
()	S_2	$HOMO-1 \rightarrow LUMO$	451	0.0080	
	S_3	$HOMO-2 \rightarrow LUMO^a$	442	0.0016	
	S_4	$HOMO-3 \rightarrow LUMO$	414	0.0043	
	S_5	$HOMO-4 \rightarrow LUMO$	361	0.5147	
(E)- 3b	S_1	$HOMO \rightarrow LUMO$	539	0.0000	
· /	S_2	$HOMO-1 \rightarrow LUMO$	482	0.0646	
	S_3	$HOMO-3 \rightarrow LUMO$	440	0.0023	
	S_4	$HOMO-2 \rightarrow LUMO^a$	429	0.0780	
	S_5	$\rm HOMO{-4} \rightarrow \rm LUMO$	367	0.3196	
^{<i>a</i>} There is more coefficients.	tha	in one transition with	almost equ	uvalent CI	

strength, these transitions mainly contribute to the UV-vis spectrum of (E)-**1b**·W(CO)₅. Thus, the spectrum is similar to that of metal-free (E)-**1b**,⁴ which also corresponds to the n– π * and π – π * transitions of the azobenzene (Fig. 5).

Thirdly, in (*E*)-**3b**, the HOMO corresponds to bonding orbitals of Pt–C bond in addition to the p orbital of chlorine. The HOMO–1 and HOMO–2 consist of the π orbital of the azobenzene and d orbital of the platinum. The LUMO is mainly the π^* orbital of the azobenzene with a small contribution of the d orbital of the platinum. These orbitals can reasonably be understood as hybridization of the molecular orbitals of 2-diphenylphosphinoazobenzene⁴ and the Pt–Cl unit. The TD-DFT calculations show contribution of both HOMO–1 \rightarrow LUMO and HOMO–2 \rightarrow LUMO transitions, which have π – π^* transition characters, to the absorption in addition to the HOMO \rightarrow LUMO transition. The absorptions of (*E*)-**3b** are assigned to both π – π^* transition and metal-to-ligand charge transfer absorptions from a Pt^{II} d orbital to a π^* orbital of the azobenzene, which coordinates directly to the platinum.¹³

The different absorptions of these three complexes originate both in the structural difference of the ambidentate ligand and in the metal fragment.

Conclusions

In conclusion, 2-phosphinoazobenzenes in equilibrium with inner phosphonium salts were utilized as ambidentate ligands or multidentate ligands toward some metals. Their reactions with hard and soft metals gave the amide and the phosphine complexes, respectively. The change in nature of metals successfully provided the different coordination modes of the ligand in the resulting complexes. The different coordination modes of the ligand in the metal complexation led to control of the properties of the 2-diphenylphosphinoazobenzene such as UV-vis absorption and stability to hydrolysis. The versatile coordination modes, which have an influence on properties of some metal catalysts, of a single ligand will be an advantage in preparation of metal catalysts.

Solvents, reagents and techniques

Solvents were purified and dried by an MBraun solvent purification system or fractional distillation. All reactions were carried out under argon atmosphere in a glovebox or in a sealed NMR tube unless otherwise noted. The ¹H NMR and ¹³C{¹H} NMR spectra were measured with JEOL AL400, Bruker AV300 and Bruker DRX500 spectrometers using tetramethylsilane as an external standard. The ³¹P NMR spectra were measured with a JEOL A500 spectrometer using tributylphosphine ($\delta_{\rm P} = -31.8$) as an external standard. The UV-vis spectra were measured with a JASCO V-530 spectrophotometer and 10 mm quartz cell. All melting points are uncorrected. FAB-Mass spectral data were obtained on a JEOL JMS-SX102 spectrometer. Elemental analyses were performed by the Microanalytical Laboratory of Department of Chemistry, Faculty of Science, The University of Tokyo. Compounds (E)-1a and (E)-1b were prepared according to the literature.⁴

Synthesis of (E)-2a·ZnCl₂·(THF)

To (*E*)-1a (65.6 mg, 0.18 mmol) in THF (0.5 mL) was added zinc chloride (28.0 mg, 0.18 mmol), and the reaction solution was stirred at room temperature for 5 min. Recrystallization from the reaction solution gave orange crystals. The precipitate was filtrated, washed with THF, and dried *in vacuo* to give yellow-orange crystals of 2a·ZnCl₂ (92.4 mg, 90%).

Spectral and analytical data for $2a \cdot 2n \cdot Cl_2 \cdot (THF)$: m.p. 158.0–159.0 °C. ¹H NMR (C₆D₆, 300 MHz) δ 1.36–1.45 (m, 4H), 3.53–3.60 (m, 4H), 6.24–6.33 (m, 1H), 6.60 (t, J = 7.8 Hz, 1H), 6.69 (t, J = 8.4 Hz, 1H), 6.82 (t, J = 7.8 Hz, 2H), 6.85–6.92 (m, 2H), 6.95–7.10 (m, 5H), 7.39 (d, J = 8.4 Hz, 2H), 7.52 (dd, J = 13.8, 7.2 Hz, 4H), 8.06 (dd, J = 8.7, 4.5 Hz, 1H). ³¹P NMR (162 MHz, THF) δ 42.7 (br s). A reasonable ¹³C NMR spectrum could not be obtained because of its quite low solubility. Anal. Calcd for C₂₈H₂₇N₂Cl₂OPZn, C, 58.51; H, 4.73; N, 4.87. Found C, 58.57; H, 4.86; N, 4.68%.

Synthesis of (E)-1b·W(CO)₅

To a solution of W(CO)₅(THF), which was prepared *in situ* from W(CO)₆ (180 mg, 0.51 mmol) in THF (10 mL), was added a THF solution (5 mL) of (*E*)-**1b** (75 mg, 0.19 mmol) and the reaction solution was stirred at r.t. for five hours. After evaporation of the solvent, separation by silica gel chromatography (eluent: CHCl₃) gave orange solid of (*E*)-**1b**·W(CO)₅ (130 mg, 75%).

Spectral and analytical data for (*E*)-**1**b·W(CO)₅: m.p. 189.0–190.0 °C. ¹H NMR (500 MHz, CDCl₃) δ 2.27 (s, 3H), 2.32 (s, 3H), 6.69 (dd, *J* = 8.0 Hz, *J* = 0.8 Hz, 1H), 6.98–7.04 (m, 4H), 7.32 (dd, *J* = 8.0 Hz, *J* = 1.8 Hz, 1H), 7.35–7.41 (m, 6H), 7.58–7.65 (m, 4H), 7.86 (dd, *J* = 8.0 Hz, *J* = 4.5 Hz, 1H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 21.50 (s, *C*H₃), 21.78 (s, *C*H₃), 115.85 (d, *J*_{CP} = 5.0 Hz, *C*H), 123.25 (s, *C*H), 128.30 (d, *J*_{CP} = 10.0 Hz, *C*H), 129.29 (s, *C*H), 129.91 (s, *C*H), 131.90 (s, *C*H), 132.48 (d, *J*_{CP} = 5.6 Hz, *C*H), 133.82 (d, *J*_{CP} = 36.3 Hz, *C*H), 135.72 (d, ¹*J*_{CP} = 42.0 Hz, *C*P), 136.55 (d, ¹*J*_{CP} = 36.3 Hz,

CP), 141.16 (d, $J_{CP} = 8.2$ Hz, CMe), 141.66 (s, CMe), 149.43 (d, $J_{CP} = 5.0$ Hz, CN), 150.35 (s, CN), 197.25 (d, $J_{CP} = 7.5$ Hz, CO), 199.27 (d, $J_{CP} = 22.3$ Hz, CO). ³¹P NMR (162 MHz, CDCl₃) δ 19.1 (s, ¹ $J_{PW} = 246.0$ Hz). FAB-MS m/z 718 (M⁺). Anal. Calcd for C₃₁H₂₃N₂O₅PW, C, 51.83; H, 3.23; N, 3.90. Found C, 52.02; H, 3.47; N, 3.77%.

Synthesis of (E)-3b

Compound (*E*)-**1b** (70 mg, 177 μ mol) and dichloro(cyclooctadiene)platinum (19.0 mg, 51 μ mol) was stirred at r.t. in dry CHCl₃ (5 mL) for 5 min. After addition of hexane to the reaction mixture, a precipitate was formed. The precipitate was filtrated, washed with hexane, and dried *in vacuo* to give a red powder of (*E*)-**3b** (77 mg, 66%).

Spectral and analytical data for (E)-3b: m.p. 256 °C (decomp.). ¹H NMR (500 MHz, CDCl₃) δ 2.35 (s, 3H), 2.53 (s, 3H), 7.11 (d, ${}^{3}J_{HH} = 7.5$ Hz, 1H), 7.42–7.53 (m, 7H), 7.74 (dd, ${}^{3}J_{\rm HP} = 11.5$ Hz, ${}^{3}J_{\rm HH} = 7.5$ Hz, 4H), 7.82 (d, ${}^{3}J_{\rm HH} = 7.5$ Hz, 1H), 8.03 (dd, ${}^{3}J_{HH} = 8.0$ Hz, $J_{HP} = 4.0$ Hz, 1H), 8.29 (dd, ${}^{3}J_{HH}$ = 8.0 Hz, $J_{\rm HP}$ = 4.0 Hz, 1H). ¹³C NMR (CDCl₃, 75 MHz) δ 21.31 (s), 23.11 (s), 119.98 (d, J_{CP} = 9.6 Hz, J_{CPt} = 19.2 Hz (satellite)), 127.70 (s), 128.39 (d, $J_{CP} = 3.3$ Hz, $J_{CPt} = 11.7$ Hz (satellite)), 129.03 (d, J_{CP} = 10.8 Hz), 129.70 (d, J_{CP} = 47.3 Hz, $J_{\rm CPt}$ = 15.0 Hz (satellite)), 131.06 (d, $J_{\rm CP}$ = 2.3 Hz), 133.10 (s, $J_{CPt} = 15.0 \text{ Hz} \text{ (satellite)}$, 133.22 (d, $J_{CP} = 1.7 \text{ Hz}$), 133.48 (d, $J_{\rm CP} = 1.7$ Hz), 133.59 (s, $J_{\rm CPt} = 13.7$ Hz (satellite)), 133.76 (s, $J_{\rm CPt}$ = 12.4 Hz (satellite)), 144.16 (d, $J_{\rm CP}$ = 5.7 Hz), 145.67 (d, $J_{\rm CP}$ = 7.2 Hz, $J_{\rm CPt}$ = 26.3 Hz), 155.38 (d, $J_{\rm CP}$ = 16.8 Hz), 164.61 (d, $J_{CP} = 49.2$ Hz), 165.44 (d, $J_{CP} = 65.1$ Hz). ³¹P NMR (162 MHz, CDCl₃) δ 30.2 (s, ${}^{1}J_{PPt} = 2072$ Hz (satellite)). Anal. Calcd for C₂₆H₂₂N₂ClPPt, C, 50.05; H, 3.55; N, 4.49. Found C, 50.00; H, 3.90; N, 4.05%.

Computational method

Calculations were performed with Gaussian 03.¹⁴ The DFT and TD-DFT^{15–17} calculations were performed with the B3LYP method.^{18,19} The 6-311+G(d,p) basis set was used for C, H, N, O, P and Cl, and LANL2DZ with effective core potentials^{20–22} for Zn, W, and Pt.

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