Supporting Information

Synthesis and Structures of Platinum(0) Alkyne Complexes with Extended π-Conjugated Systems

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Experimental Section

All manipulations were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. NMR spectra were recorded on a Varian Mercury 300 spectrometer. Chemical shifts are reported in δ, referenced to ^{1}H (of residual protons) and ^{13}C signals of deuterated solvents as internal standards or to the ^{31}P signal of 85% H_3PO_4 as an external standard. Cyclic voltammetory was performed with a BAS ALS600C Electrochemical Analyzer. UV-vis absorption spectra were measured by a JASCO V560 spectrometer. Elemental analysis was performed by the ICR Analytical Laboratory, Kyoto University. DPCB-phen was prepared by a slightly modified literature method.[1]

[Pt(dmad)(DPCB-phen)] (1a): mp 273 °C. ^{1}H NMR ($CDCl_3$, 20 °C): δ 1.50 (s, 18H), 1.66 (s, 36H), 3.74 (s, 6H), 5.30 (d, J_{HH} = 7.7 Hz, 2H), 7.12 (t, J_{HH} = 7.7 Hz, 4H), 7.48 (t, J_{HH} = 7.7 Hz, 2H), 7.62 (s, 4H), 8.44 (d, J_{HH} = 8.4 Hz, 2H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 20 °C): δ 31.6 (s), 34.0 (s), 35.4 (s), 38.7 (s), 52.1 (s), 121.5 (t, J_{PtC} = 432 Hz, J_{PC} = 45 Hz, C≡C), 122.1 (s), 123.7 (s), 124.5 (s), 125.0 (s), 127.6 (s), 127.8 (s), 129.0 (t, J_{PC} = 4 Hz), 132.2 (s), 142.9 (t, J_{PC} = 8 Hz), 152.7 (s), 157.8 (s), 162.7 (t, J_{PC} = 19 Hz), 172.8 (t, J_{PC} = 37 Hz). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 20 °C): δ 150.7 (s, J_{PtP} = 3913 Hz). IR (KBr): 2963, 1771, 1704, 1206, 754 cm^{-1}. FABMS: m/z 1090 (M^+, 100), 945 (78). Anal. Calcd. for $C_{58}H_{72}O_4P_2Pt$: C, 63.90; H, 6.66. Found: C, 63.58; H, 6.84.

[Pt(tolan-H)(DPCB-phen)] (1b): mp >290 °C. ^{1}H NMR ($CDCl_3$, 20 °C): δ 1.54 (s, 18H), 1.66 (s, 36H), 6.02 (d, J_{HH} = 8.1 Hz, 2H), 7.10-7.16 (m, 2H), 7.10–7.16 (m, 2H), 7.22 (t, J_{HH} = 7.3 Hz, 4H), 7.46 (t, J_{HH} = 8.1 Hz, 2H), 7.67 (s, 4H), 7.82 (d, 4H), 8.44 (d, J_{HH} = 8.4 Hz, 2H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 20 °C): δ 31.6 (s), 33.8 (s), 35.4 (s), 38.9 (s), 122.3 (m, C≡C), 122.3 (s), 123.7 (s), 124.9 (s), 125.1 (s), 126.7 (s), 127.1 (s), 127.4 (s), 127.9 (s), 130.8 (t, J_{PC} = 10 Hz), 131.3 (s), 131.7 (t, J_{PtC} = 48 Hz, J_{PC} = 4 Hz), 131.8 (s), 143.0 (t, J_{PC} = 6 Hz), 152.2 (s), 157.0 (s), 173.0 (dd, J_{PC} = 35 Hz, J_{PC} = 33 Hz). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 20 °C): δ 155.7 (s, J_{PtP} = 3455 Hz). IR (KBr): 2963, 1593, 1477, 756 cm^{-1}. FABMS: m/z 1126 (M^+, 100) 945 (60). Anal. Calcd. for $C_{66}H_{76}P_2Pt$: C, 70.38; H, 6.80. Found: C, 70.13; H, 6.83.

[Pt(tolan-OMe)(DPCB-phen)] (1c): mp > 290 °C. ^{1}H NMR ($CDCl_3$, 20 °C): δ 1.55 (s, 18H), 1.67 (s, 36H), 3.80 (s, 6H), 6.03 (d, J_{HH} = 8.0 Hz, 2H), 6.75 (d, J_{HH} = 8.6 Hz, 4H), 7.12 (t, J_{HH} = 7.6 Hz, 2H),

7.46 (t, J_{HH} = 7.3 Hz, 2H), 7.68 (s, 4H), 7.75 (d, J_{HH} = 8.6 Hz, 4H), 8.43 (d, J_{HH} = 8.2 Hz, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ 31.6 (s), 33.8 (s), 35.4 (s), 38.9 (s), 55.3 (s), 113.3 (s), 121.5 (t, J_{PC} = 38 Hz, C≡C), 122.3 (s), 122.5 (t, J_{PC} = 11 Hz), 123.7 (s), 124.9 (s), 125.1 (s), 127.0 (s), 127.4 (s), 131.6 (s), 131.8 (s), 133.2 (t, J_{PtC} = 56 Hz, J_{PC} = 4 Hz), 143.0 (t, J_{PC} = 6 Hz), 152.2 (s), 156.9 (s), 158.5 (s), 172.8 (t, J_{PC} = 35 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ 156.6 (s, J_{PtP} = 3436 Hz). IR (KBr): 2962, 1600, 1507, 1243, 1036, 830, 757 cm^{-1}. FABMS: m/z 1186 (M^+, 100), 945 (23). Anal. Calcd. for $C_{68}H_{80}O_2P_2Pt$: C, 68.84; H, 6.80. Found: C, 68.97; H, 6.97.

[Pt(tolan-NMe$_2$)(DPCB-phen)] (1d): mp > 290 °C. ^1H NMR ($CDCl_3$, 20 °C): δ 1.54 (s, 18H), 1.67 (s, 36H), 2.91 (s, 12H), 6.05 (d, J_{HH} = 7.9 Hz, 2H), 6.56 (d, J_{HH} = 8.7 Hz, 4H), 7.12 (t, J_{HH} = 7.5 Hz, 2H), 7.44 (t, J_{HH} = 7.5 Hz, 2H), 7.68 (s, 4H), 7.69 (d, J_{HH} = 8.7 Hz, 4H), 8.42 (d, J_{HH} = 8.3 Hz, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ 31.7 (s), 33.9 (s), 35.6 (s), 39.0 (s), 40.6 (s), 111.9 (s), 119.5 (t, J_{PC} = 11 Hz), 121.4 (t, J_{PC} = 37 Hz, C≡C), 122.2 (s), 123.6 (s), 125.0 (s), 125.1 (s), 126.7 (s), 127.3 (s), 132.3 (s), 132.2 (s), 133.2 (t, J_{PtC} = 58 Hz, J_{PC} = 4 Hz), 142.9 (t, J_{PC} = 7 Hz), 149.2 (s), 151.9 (s), 156.9 (s), 172.2 (t, J_{PC} = 34 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ 157.4 (s, J_{PtP} = 3406 Hz). IR (KBr): 2961, 1602, 1516, 1362, 1124, 816, 755 cm^{-1}. FABMS: m/z 1212 (M^+, 100), 945 (23). Anal. Calcd. for $C_{70}H_{86}N_2P_2Pt$: C, 69.34; H, 7.15; N, 2.31. Found: C, 69.42; H, 7.05; N, 2.27.

X-ray Crystal Structure Determination of 1c. A single crystal of dimensions 0.21 × 0.17 × 0.10 was grown by slow diffusion of a CH_2Cl_2 solution to MeOH at room temperature. The intensity data were collected on a Rigaku Mercury CCD diffractometer at 173 K using Mo K_α radiation (λ = 0.71070 Å). The data was corrected for Lorentz and polarization effects and absorption (REQAB). The structure was solved by direct methods (SHELXS-97) and refined on F^2 against all reflections (SHELXL-97).[2] Further information has been deposited with the Cambridge Crystallographic Data Centre (CCDC-661220). Crystallographic data are summarized in Table S1.

References

(1) Nakamura, A.; Kawasaki, S.; Toyota, K.; Yoshifuji, M. *Chem. Lett.* **2004**, *33*, 1570.

(2) Sheldrick, G. M. *SHELXL-97*; University of Gottingen: Germany, 1997.

Table S1. Crystallographic Data for 1c

color	purple
habit	block
crystal size (mm)	0.21 × 0.17 × 0.10
formula	$C_{68}H_{80}O_2P_2Pt$
formula weight	1186.35
crystal system	monoclinic
a (Å)	14.684(3)
b (Å)	22.008(4)
c (Å)	18.693(3)
β (deg)	107.720(2)
V (Å^3)	5754.3(18)
space group	$P2_1/c$ (No. 14)
Z	4
d_{calcd} (g cm^{-3})	1.369
μ(Mo *K*α) (mm^{-1})	2.538
transmission factor	0.6177–0.7854
θ range (deg)	3.00–27.48
no. of reflns collected	45340
no. of independent reflns	13140 [R_{int} = 0.0347]
no. of reflns with $I > 2\sigma(I)$	11936
no. of variables	898
goodness-of-fit on F^2	1.085
final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0266, wR_2 = 0.0586
R indices (all data)	R_1 = 0.0319, wR_2 = 0.0610