Articles

Bis(2,6-dinitroaryl)platinum(II) Complexes. Cis/Trans Isomerization†

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The complexes *cis*-[Pt(κ^2-Aryl)(κ^1-Aryl)L] (κ^2-Aryl = κ^2-(*C*,*O*)-$C_6(NO_2)_2$-2,6-$(OMe)_3$, κ^1-Aryl = κ^1-(*C*)-$C_6(NO_2)_2$-2,6-$(OMe)_3$, L = *S*-dmso (**2*cis***), XyNC (**4*cis***; Xy = 2,6-$Me_2C_6H_4$), CO (**5*cis***), PPh_3 (**7*cis***)) have been obtained by reacting at room temperature *cis*-[Pt(κ^2-Aryl)(κ^1-Aryl)(OH_2)] (**1*cis***) with dimethyl sulfoxide (dmso; 1:1 or excess), XyNC (1:1), or CO (excess) or *cis*-(Me_4N)[Pt(κ^2-Aryl)(κ^1-Aryl)Cl] with PPh_3 (1:1), respectively. The room-temperature reaction of **1*cis*** with XyNC (1:2), of **5*cis*** with PPh_3 (1:1), or of *cis*-(Me_4N)[Pt(κ^2-Aryl)(κ^1-Aryl)Cl] with PPh_3 (1:2) gives *cis*-[Pt(κ^1-Aryl)$_2$LL′] (L = L′ = XyNC (**3*cis***), PPh_3 (**8*cis***); L = CO, L′ = PPh_3 (**6*cis***)). Complexes **3*cis***, **4*cis***, and **5*cis*** isomerize on heating in solution or in the solid state to give **3*trans***, **4*trans***, and **5*trans***, respectively, while **6*cis*** and **8*cis*** decompose to give **7*cis*** instead of their trans isomers; these, however, can be prepared by reacting **5*trans*** or **6*trans*** with PPh_3 in molar ratios of 1:1 or 1:2, respectively. When they are heated, **6*trans*** and **8*trans*** also descompose to **7*cis***, while **2*cis*** and *cis*-[Pt(κ^2-Aryl)(κ^1-Aryl)L] (L = H_2O (**1*cis***), PhCN, tht) decompose to a mixture of unidentified products (**1*cis***) or are recovered unchanged. These results, and others reported in the literature, on the stability of *cis*- and *trans*-diaryl complexes of platinum or palladium can be explained as the result of two competing factors, transphobia and the steric requirements of the ligands. The X-ray crystal structures of **2*cis***, **3*cis***, **3*trans***, **4*trans***·$CHCl_3$, **5*cis***·CH_2Cl_2, **5*cis***·0.5hexane, **6*cis***, **6*trans***·$CHCl_3$, **7*cis***·Me_2CO, and **8*trans***·0.5$CHCl_3$ have been determined.

Introduction

The cis/trans isomerization of square-planar platinum(II) complexes is still a subject of great interest. Thus, in agreement with the claim that *cis*-diorganoplatinum complexes are thermodynamically more stable than the corresponding trans isomers,[1,2] van Koten et al.[2] reported last year that the presence of ortho substituents in [Pt(C∧N)$_2$] complexes, where C∧N is a (dimethylamino)methylaryl ligand, favors the formation of the cis isomers, even when starting from *trans*-[$PtCl_2(SMe_2)_2$], and that the trans isomers isomerize irreversibly to the thermodynamically favored cis isomers upon heating. Almost simultaneously, Klein et al.[3] reached apparently opposite conclusions: the complexes [Pt(aryl)$_2$(*S*-dmso)$_2$] (dmso = dimethyl sulfoxide), obtained by reacting *cis*-[$PtCl_2$(dmso)$_2$)] with the corresponding [Sn(aryl)Me_3] compound at 90−100 °C, have a trans geometry when aryl = 2,3,4,5,6-pentamethylphenyl, 2,4,6-trimethylphenyl, 2,6-dimethylphenyl and a cis geometry for those complexes with phenyl and 2-tolyl ligands. DFT calculation results agreed well with the experimental data.[3] These complexes react in refluxing toluene with PEt_3 to give [Pt(aryl)$_2$(PEt_3)$_2$] with the same geometry as the dmso precursors.[4]

The above controversy gives a good picture of how we have failed to understand the relative stability of geometric isomers in Pt(II) complexes and, in particular, of the diaryl derivatives. The reasons for this situation are the limited studies devoted to isomerization reactions and the inertness of Pt(II) complexes. The latter means that the isolated complex in many reactions at moderate temperatures and reaction times is usually the kinetic product, often with retention of the geometry around the platinum center, but not the thermodynamic product.[5] Thus, *cis*- or *trans*-[Pt(*o*-tolyl)$_2$(PEt_3)$_2$] could be prepared by reacting *cis*- or *trans*-[$PtCl_2$(PEt_3)$_2$], respectively, with 2-tolyllithium at room temperature.[6] In addition, the complex *cis*-[Pt(C_6F_5)$_2$(CO)(tht)], obtained from *cis*-[Pt(C_6F_5)$_2$(tht)$_2$] and *cis*-[Pt(C_6F_5)$_2$(CO)$_2$],[7] has

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† Dedicated to Dr. Jose-Antonio Abad, with best wishes, on the occasion of his retirement.

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(1) Brune, H. A.; Schmidtberg, G.; Wiege, M. *Z. Naturforsch., B* **1984**, *39*, 517. Hoogervorst, W. J.; Koster, A. L.; Lutz, M.; Spek, A. L.; Elsevier, C. J. *Organometallics* **2004**, *23*, 1161. Jawad, J. K.; Puddephatt, R. J.; Stalteri, M. A. *Inorg. Chem.* **1982**, *21*, 332.

(2) Amijs, C. H. M.; van Klink, G. P. M.; Lutz, M.; Spek, A. L.; van Koten, G. *Organometallics* **2005**, *24*, 2944.

(3) Klein, A.; Schurr, T.; Knödler, A.; Gudat, D.; Klinkhammer, K. W.; Jain, V. K.; Zalis, S.; Kaim, W. *Organometallics* **2005**, *24*, 4125.

(4) Gudat, D.; Jain, V. K.; Klein, A.; Schurr, T.; Zális, S. *Eur. J. Inorg. Chem.* **2005**, 4056.

(5) Falvello, L. R.; Fornies, J.; Gomez, J.; Lalinde, E.; Martin, A.; Martínez, F.; Moreno, M. T. *Dalton Trans.* **2001**, 2132. Ara, I.; Falvello, L. R.; Fornies, J.; Lalinde, E.; Martin, A.; Martínez, F.; Moreno, M. T. *Organometallics* **1997**, *16*, 5392.

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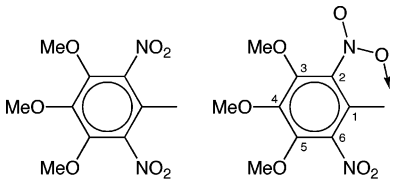
Chart 1



κ^1-Aryl κ^2-Aryl

been used to prepare other *cis*-[Pt(C_6F_5)$_2$LL′] complexes.[7−9] However, recently *trans*-[Pt(C_6F_5)$_2$(CO)(tht)] has been obtained by heating the cis isomer in benzene or cyclohexane.[10]

In agreement with the above data, the much greater number of reported crystal structures of *cis*-diarylplatinum(II) complexes (173) as compared to the number of those for *trans*-diarylplatinum(II) (23) complexes[11] cannot be used as evidence for the greater stability of the cis isomers. To establish the characteristics that stabilize *cis*- or *trans*-diarylplatinum(II), we have selected (i) those characterized by X-ray diffraction studies,[12] (ii) those whose geometry is not imposed by the other ligands, and (iii) those that were obtained by prolonged heating of the reactants. The 11 *trans*-diarylplatinum(II) complexes obtained under these conditions are [Pt(R)(R′)(PR″$_3$)$_2$] (R = R′ = C_6H_4-CF_3-4,[13] 2,6-$Me_2C_6H_3$, 2,4,6-$Me_3C_6H_2$[4] (R″ = Et), 2,4,6-$(MeO)_3C_6H_2$,[14] 3,5-$(CF_3)_2C_6H_3$,[15] Ph[16] (R″ = Ph); R = Ph, α-biphenylenyl, R′ = α-biphenyl (R″ = Et), [Pt(2,2′-tetraphenyl)(PEt$_3$)$_2$]),[17] and [PtR$_2$(*S*-dmso)$_2$] (R = $C_6H_3Me_2$-2,6, C_6H_2-Me_3-2,4,6).[3] The 9 *cis*-diarylplatinum(II) complexes are 3 of the type [PtR$_2$L$_2$] (L = *S*-dmso, R = Ph,[18] 2-tolyl;[3] L = PEt$_3$, R = Ph),[4] the 6 orthoplatinated complexes [Pt(C∧X)(C′∧X′)] (C∧X = C′∧X′ = 2-X-R: X = NHPPh$_2$, R = C_6H_4;[19] X = CH_2NMe_2, R = 1-naphthyl, C_6H_2Br-4-CH_2NMe_2-5;[2] X = $CH_2P(CH_2Ph)_2$, R = C_6H_4;[20] C∧X: X = PPh$_2$, R = C_6H_4; C′∧X′: X′ = PPh$_2$(HgCl)C_6H_4PPh$_2$-2, R = C_6H_4),[21] and [Pt(C∧X)(R)Cl]$^-$ (C∧X = κ^2-Aryl, R = κ^1-Aryl; see Chart 1).[22] In this paper we present new data and the factors that influence the stability of diarylplatinum(II) complexes.

We are involved in the study of the reactivity of organomercury complexes as transmetalating agents.[23] In this context, we have recently reported the synthesis of the diaryl complex *cis*-(Me_4N)[Pt(κ^2-Aryl)(κ^1-Aryl)Cl] by high-temperature transmetalation from [Hg(κ^1-Ar)$_2$] and [PtCl$_4$]$^{2-}$ and of some of their derivatives, *cis*-(Me_4N)[Pt(κ^2-Aryl)(κ^1-Ar)(*O*,*O*-acac)] and [Pt(κ^2-Aryl)(κ^1-Ar)L] (L = H_2O (**1*cis***), PhCN, tetrahydrothiophene), as well as a family of complexes containing Pt−Hg bonds. All of these bis(2,6-dinitroaryl)platinum complexes had a cis geometry.[22,24] Here we report the syntheses of new *cis*-bis(2,6-dinitroaryl)platinum complexes and a study of their thermal stability that has allowed us to prepare some of their trans isomers. The latter have been used to prepare, by ligand substitution, other *trans*-diaryl complexes not accessible by thermal isomerization. The study of the thermal stability of these complexes has allowed us to observe decomposition reactions, not involving the C−Pt bonds, that lead to a *cis*-diaryl complex. This has given us more data to formulate the factors that promote the stability of *cis*- or *trans*-diaryl complexes of group 10 metals and, consequently, to predict which of them would be easily isomerized. However, it is important to realize that the thermal isomerizations have been observed because the presence of the two nitro groups in the ortho positions of the aryl ligands confers on them a remarkably high thermal stability.

Experimental Section

Unless otherwise stated, the reactions were carried out without precautions to exclude light or atmospheric oxygen or moisture. The IR (Nujol/polyethylene), C, H, and N analyses, and melting point determinations were carried out as described elsewhere.[25] NMR spectra were recorded on Varian Unity 300, Bruker AC 200, Avance 300 and 400, and Bruker 600 spectrometers at room temperature unless otherwise stated. Chemical shifts were referenced to TMS (^{1}H, ^{13}C{^{1}H}) or H_3PO_4 (^{31}P{^{1}H}). The NMR probe temperature was calibrated using ethylene glycol ^{1}H NMR standard methods. The complex *cis*-(Me_4N)[Pt(κ^2-Aryl)(κ^1-Aryl)Cl] and CH_2Cl_2 and Et_2O solutions of *cis*-[Pt(κ^2-Aryl)(κ^1-Aryl)(OH_2)] (**1*cis***) were prepared as reported previously.[22] The aryl group $C_6(NO_2)_2$-2,6-$(OMe)_3$ and the ligands κ^1-(*C*)-$C_6(NO_2)_2$-2,6-$(OMe)_3$ and κ^2-(*C*,*O*)-$C_6(NO_2)_2$-2,6-$(OMe)_3$ are represented by Aryl, κ^1-Aryl, and κ^2-Aryl (see Chart 1).

Synthesis of *cis*-[Pt(κ^2-Aryl)(κ^1-Aryl)(dmso)] (2*cis*). To a stirred solution of **1*cis*** (0.12 mmol) in CH_2Cl_2 (5 mL) was added dmso (9.15 mg, 0.12 mmol). The resulting solution was concentrated to dryness, and Et_2O (20 mL) was added to give a suspension, which was filtered to give an orange solid that was washed with Et_2O and identified as **2*cis*** (48 mg). The filtrate was concentrated (2 mL), *n*-hexane (2 mL) was added, and the suspension was filtered to give a solid that was washed with *n*-hexane to give a second crop of **2*cis*** (41 mg). Yield: 89 mg, 96%. Mp: 188−192 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.07 (s, 6 H, OMe), 4.04 (s, 3 H, OMe), 4.02 (s, 3 H, OMe), 3.91 (s, 3 H, OMe), 3.84 (s, 3 H, OMe), 3.24 (s + d, 6 H, Me, $^3J_{PtH}$ = 13,5 Hz). ^{13}C{^{1}H} NMR (100.81 MHz, $CDCl_3$, 25 °C): δ 154.83 (*m*-C κ^2-Aryl), 154.00 (*m*-C κ^2-

(6) Chatt, J.; Shaw, B. L. *J. Chem. Soc.* **1959**, 808. Rieger, A. L.; Carpenter, G. B.; Rieger, P. H. *Organometallics* **1993**, *12*, 842.
(7) Uson, R.; Fornies, J.; Espinet, P.; Fortuno, C.; Tomas, M.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1988**, 3005.
(8) Ara, I.; Berenguer, J. R.; Forniés, J.; Lalinde, E.; Tomás, M. *Organometallics* **1996**, *15*, 1014.
(9) Berenguer, J. R.; Forniés, J.; Lalinde, E.; Martínez, F. *Organometallics* **1995**, *14*, 2532.
(10) Berenguer, J. R.; Fornies, J.; Martin, L. F.; Martin, A.; Menjon, B. *Inorg. Chem.* **2005**, *44*, 7265.
(11) CSD version 5.26 (May 2005).
(12) We only consider complexes characterized by X-ray diffraction studies because some studied only by NMR were later corrected.[3]
(13) Mintcheva, N.; Nishihara, Y.; Tanabe, M.; Hirabayashi, E.; Mori, A.; Osakada, K. *Organometallics* **2001**, *20*, 1243.
(14) Brune, H. A.; Wiege, M.; Debaerdemaeker, T. *Z. Naturforsch., B* **1984**, *39*, 907.
(15) Konze, W. V.; Scott, B. L.; Kubas, G. J. *Chem. Commun.* **1999**, 1807.
(16) Ertl, J.; Debaerdemaeker, T.; Brune, H. A. *Chem. Ber.* **1982**, *115*, 3860.
(17) Edelbach, B. L.; Lachicotte, R. J.; Jones, W. D. *J. Am. Chem. Soc.* **1998**, *120*, 2843.
(18) Bardi, R.; Del Pra, A.; Piazzesi, A. M.; Trozzi, M. *Cryst. Struct. Commun.* **1981**, *10*, 301.
(19) Gaw, K. G.; Slawin, A. M. Z.; Smith, M. B. *Organometallics* **1999**, *18*, 3255.
(20) Porzio, W. *Inorg. Chim. Acta* **1980**, *40*, 257.
(21) Bennett, M. A.; Contel, M.; Hockless, D. C. R.; Welling, L. L.; Willis, A. C. *Inorg. Chem.* **2002**, *41*, 844.
(22) Vicente, J.; Arcas, A.; Gálvez-López, M. D.; Jones, P. G. *Organometallics* **2004**, *23*, 3521.
(23) Vicente, J.; Chicote, M. T.; Arcas, A.; Artigao, M. *Inorg. Chim. Acta* **1982**, *65*, L251. Vicente, J.; Arcas, A.; Fernández-Hernández, J. M.; Sironi, A.; Masciocchi, N. *Chem. Commun.* **2005**, 1267. Vicente, J.; Arcas, A.; Fernández-Hernández, J. M.; Bautista, D. *Organometallics* **2001**, *20*, 2767. Vicente, J.; Chicote, M. T.; Ramírez-de-Arellano, M. C.; Pelizzi, G.; Vitali, F. *J. Chem. Soc., Dalton Trans.* **1990**, 279. Vicente, J.; Martin, J.; Solans, X.; Font-Altaba, M. *Organometallics* **1989**, *8*, 357. Vicente, J.; Abad, J. A.; Rink, B.; Hernández, F.-S.; Ramírez de Arellano, M. C. *Organometallics* **1997**, *16*, 5269.
(24) Vicente, J.; Arcas, A.; Gálvez-López, M. D.; Jones, P. G. *Organometallics* **2004**, *23*, 3528.
(25) Vicente, J.; Chicote, M. T.; Huertas, S.; Bautista, D.; Jones, P. G.; Fischer, A. K. *Inorg. Chem.* **2001**, *40*, 2051.

Aryl), 148.33 (*m*-C κ^1-Aryl, $^3J_{PtC}$ = 68 Hz), 147.32 (*o*-C κ^1-Aryl), 147.02 (*o*-C κ^2-Aryl), 144.84 (*p*-C κ^2-Aryl), 143.84 (*p*-C Aryl), 136.82 (*o*-C κ^2-Aryl), 128.40 (*i*-C Aryl), 110.86 (*i*-C Aryl), 62.35 (*m*-OMe), 62.19 (*m*-OMe), 61.64 (*p*-OMe), 61.29 (*p*-OMe), 42.92 (Me, $^2J_{PtC}$ = 32 Hz). Anal. Calcd for $C_{20}H_{24}N_4O_{15}PtS$: C, 30.50; H, 3.07; N, 7.11; S, 4.07. Found: C, 30.18; H, 3.06; N, 7.16; S, 3.67. Single crystals of **2*cis*** were obtained by slow diffusion of *n*-hexane into an acetone solution of **2*cis***.

Synthesis of *cis*-[Pt(κ^1-Aryl)$_2$(CNXy)$_2$] (3*cis*). To a solution of **1*cis*** (0.25 mmol) in CH_2Cl_2 (4 mL) was added XyNC (Xy = 2,6-dimethylphenyl; 65 mg, 0.50 mmol), and the resulting solution was concentrated (2 mL). Addition of Et_2O (10 mL) gave a suspension, which was filtered off; the solid was washed with Et_2O and air-dried in vacuo to give **3*cis*** as a pale yellow solid. Yield: 225 mg, 94%. Dec pt: 240 °C. IR (cm^{-1}): ν(C≡N) 2199, 2179. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.27−7.22 (m, 2 H, *p*-H Xy), 7.09−7.07 (m, 4 H, *m*-H Xy), 3.94 (s, 12 H, OMe), 3.90 (s, 6 H, OMe), 2.29 (s, 12 H, Me). ^{13}C{^{1}H} NMR (100.81 MHz, $CDCl_3$): δ 148.43 (*o*-C Aryl, $^2J_{PtC}$ = 15 Hz), 147.39 (*m*-C Aryl, $^3J_{PtC}$ = 53 Hz), 143.89 (*p*-C Aryl), 135.86 (*o*-C Xy), 135.59 (br, C≡N), 130.08 (*p*-CH Xy), 128.12 (*m*-CH Xy), 125.74 (br, *i*-C Xy), 122.64 (*i*-C Aryl, $^1J_{PtC}$ = 880 Hz), 62.27 (*m*-OMe), 61.13 (*p*-OMe), 18.29 (Me). Anal. Calcd for $C_{36}H_{36}N_6O_{14}Pt$: C, 44.49; H, 3.73; N, 8.65. Found: C, 44.38; H, 3.70; N, 8.74. Crystals of **3*cis***·$CHCl_3$ suitable for X-ray diffraction studies were obtained by slow diffusion of *n*-hexane into a solution of **3*cis*** in $CDCl_3$.

Synthesis of *trans*-[Pt(κ^1-Aryl)$_2$(CNXy)$_2$] (3*trans*). A solution of **1*cis*** (0.15 mmol) in CH_2Cl_2 (2 mL) was concentrated to dryness, and XyNC (40 mg, 0.30 mmol) in toluene (5 mL) was then added. The resulting pale yellow suspension was stirred at 150 °C for 75 min in a Carius tube and then concentrated to dryness. CH_2Cl_2 (2 mL) and Et_2O (10 mL) were added, and the precipitate was filtered off, washed with Et_2O, and air-dried, to give **3*trans*** as a pale yellow solid. Yield: 83 mg, 56%. Dec pt: 326 °C. IR (cm^{-1}): ν(C≡N) 2196. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.23−7.18 (m, 2 H, *p*-H Xy), 7.07−7.04 (m, 4 H, *m*-H Xy), 3.95 (s, 12 H, OMe), 3.90 (s, 6 H, OMe), 2.33 (s, 12 H, Me). ^{13}C{^{1}H} NMR (75.45 MHz, $CDCl_3$): δ 148.84 (*o*-C Aryl), 146.83 (*m*-C Aryl, $^3J_{PtC}$ = 38 Hz), 143.34 (*p*-C Aryl), 136.31 (*o*-C Xy), 134.70 (br, C≡N), 130.01 (*p*-C Xy), 127.92 (*m*-C Xy), 125.50 (*i*-C Xy), 124.50 (*i*-C Aryl, $^1J_{PtC}$ = 640 Hz), 62.16 (*m*-OMe), 61.13 (*p*-OMe), 18.14 (Me). Anal. Calcd for $C_{36}H_{36}N_6O_{14}Pt$: C, 44.49; H, 3.73; N, 8.65. Found: C, 44.64; H, 4.12; N, 8.60. Single crystals of **3*trans*** were obtained by slow diffusion of Et_2O into a solution of **3*trans*** in $CHCl_3$.

Synthesis of *cis*-[Pt(κ^2-Aryl)(κ^1-Aryl)(CNXy)] (4*cis*). Method a. To a stirred solution of **1*cis*** (0.09 mmol) in CH_2Cl_2 (2 mL) was slowly added a solution of XyNC (11 mg, 0.08 mmol) in CH_2Cl_2 (15 mL) over 1 h. The solution was concentrated to dryness, the residue was stirred with Et_2O (5 mL), and the resulting suspension was filtered. The solid was washed with Et_2O and air-dried to give **4*cis*** as an orange solid. The filtrate was concentrated (2 mL), and *n*-pentane (10 mL) was added to give a second crop of **4*cis***. Yield: 54 mg, 76%.

Method b. A solution of XyNC (10 mg, 0.08 mmol) in CH_2Cl_2 (20 mL) was slowly added (for 1 h) to a stirred solution of **5*cis*** (50 mg, 0.07 mmol) in CH_2Cl_2 (2 mL). The resulting solution was concentrated to dryness, the residue was stirred with Et_2O (2 mL), and the resulting suspension was concentrated (1 mL). *n*-Pentane was added, the suspension was filtered, and the solid was washed with *n*-pentane and air-dried to give **4*cis*** as an orange solid. Yield: 26 mg, 52%. Mp: 181−182 °C. IR (cm^{-1}): ν(C≡N) 2188. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.27−7.21 (m, 1 H, *p*-H Xy), 7.10−7.08 (m, 2 H, *m*-H Xy), 4.05 (s, 6 H, OMe), 4.04 (s, 3 H, OMe), 4.02 (s, 3 H, OMe), 3.94 (s, 3 H, OMe), 3.86 (s, 3 H, OMe), 2.34 (s, 6 H, Me). ^{13}C{^{1}H} NMR (75.45 MHz, $CDCl_3$): δ 154.35 (*m*-C κ^2-Aryl), 153.80 (*m*-C κ^2-Aryl), 148.01 (*o*-C Aryl, $^2J_{PtC}$ = 31 Hz), 147.29 (*m*-C κ^1-Aryl, $^3J_{PtC}$ = 74 Hz), 144.07 (*p*-C Aryl), 144.00 (*p*-C Aryl), 137.32 (*o*-C Aryl), 136.10 (*o*-C Xy), 135.84 (br, C≡N), 130.05 (*p*-C Xy), 128.11 (*i*-C Aryl), 128.05 (*m*-C Xy), 125.61 (br, *i*-C Xy), 105.13 (*i*-C Aryl, $^1J_{PtC}$ = 1145 Hz), 62.29 (*m*-OMe κ^1-Aryl), 62.23 (*m*-OMe), 62.07 (*m*-OMe), 61.54 (*p*-OMe), 61.28 (*p*-OMe), 18.33 (Me). Anal. Calcd for $C_{27}H_{27}N_5O_{14}Pt$: C, 38.58; H, 3.24; N, 8.33. Found: C, 38.43; H, 3.18; N, 8.39.

Synthesis of *trans*-[Pt(κ^2-Aryl)(κ^1-Aryl)(CNXy)] (4*trans*). To a stirred solution of **5*trans*** (96 mg, 0.13 mmol) in CH_2Cl_2 (2 mL) was slowly added (for 1 h) a solution of XyNC (17 mg, 0.13 mmol) in CH_2Cl_2 (20 mL). The resulting solution was concentrated to dryness, and the residue was stirred with Et_2O (10 mL) in a cold bath (ice/water). The resulting suspension was filtered, the filtrate was concentrated to dryness, and Et_2O (1 mL) and *n*-pentane (3 mL) were added. The suspension was filtered off, and the solid was washed with pentane and air-dried to give **4*trans*** as an orange solid. Yield: 55 mg, 50%. Mp: 214−216 °C. IR (cm^{-1}): ν(C≡N) 2194. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.22−7.17 (m, 1 H, *p*-H Xy), 7.12−7.09 (m, 2 H, *m*-H Xy), 4.03 (s, 12 H, OMe), 3.88 (s, 6 H, OMe), 2.46 (s, 6 H, Me). ^{1}H NMR (400.91 MHz, CD_2Cl_2, −60 °C): δ 7.23−7.19 (m, 1 H, *p*-H Xy), 7.13−7.11 (m, 2 H, *m*-H Xy), 4.12 (s, 3 H, OMe), 4.02 (s, 3 H, OMe), 3.90 (s, 6 H, OMe), 3.81 (s, 3 H, OMe), 3.77 (s, 3 H, OMe), 2.37 (s, 6 H, Me). ^{13}C{^{1}H} NMR (75.45 MHz, $CDCl_3$): δ 151.11 (br, C Aryl), 144.54 (br, C Aryl), 143.72 (C Aryl), 135.75 (*o*-C Xy), 129.42 (*p*-C Xy), 127.79 (*m*-C Xy), 126.90 (br, *i*-C Xy), 113.40 (br, *i*-C Aryl), 62.22 (*m*-OMe), 61.37 (*p*-OMe), 18.25 (Me). Anal. Calcd for $C_{27}H_{27}N_5O_{14}Pt$: C, 38.58; H, 3.24; N, 8.33. Found: C, 38.22; H, 3.11; N, 8.39. Single crystals of **4*trans*** were obtained by slow diffusion of *n*-pentane into a solution of **4*trans*** in $CDCl_3$.

Synthesis of *cis*-[Pt(κ^2-Aryl)(κ^1-Aryl)(CO)] (5*cis*). A stream of CO was bubbled at atmospheric pressure into a solution of **1*cis*** (0.32 mmol) in CH_2Cl_2 (5 mL) until the red color of the solution changed to yellow. The mixture was filtered though Celite and $MgSO_4$, the filtrate was concentrated (2 mL), and *n*-hexane (10 mL) was added. The suspension was filtered, and the solid was washed with *n*-hexane and air-dried to give **5*cis*** as a yellow solid. Yield: 215 mg, 92%. Mp: 160−162 °C. IR (cm^{-1}): ν(C≡O) 2128. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.08 (s, 6 H, OMe), 4.05 (s, 3 H, OMe), 4.04 (s, 3 H, OMe), 3.96 (s, 3 H, OMe), 3.86 (s, 3 H, OMe). ^{13}C{^{1}H} NMR (100.81 MHz, $CDCl_3$, 25 °C): δ 170.28 (CO, $^1J_{PtC}$ = 1251 Hz), 154.73 (*m*-C κ^2-Aryl, $^3J_{PtC}$ = 44 Hz), 153.98 (*m*-C κ^2-Aryl, $^3J_{PtC}$ = 70 Hz), 148.32 (*m*-C κ^1-Aryl, $^3J_{PtC}$ = 71 Hz), 147.43 (*o*-C κ^1-Aryl, $^2J_{PtC}$ = 23 Hz), 146.71 (*o*-C κ^2-Aryl, $^2J_{PtC}$ = 47 Hz), 145.44 (*p*-C Aryl), 144.95 (*p*-C Aryl), 136.82 (*o*-C κ^2-Aryl, $^2J_{PtC}$ = 51 Hz), 133.98 (*i*-C κ^2-Aryl, $^1J_{PtC}$ = 977 Hz), 101.02 (*i*-C κ^1-Aryl, $^2J_{PtC}$ = 1115 Hz), 62.40 (*m*-OMe κ^2-Aryl), 62.34 (*m*-OMe κ^1-Aryl), 62.25 (*m*-OMe κ^2-Aryl), 61.71 (*p*-OMe), 61.25 (*p*-OMe). Anal. Calcd for $C_{19}H_{18}N_4O_{15}Pt$: C, 30.95; H, 2.46; N, 7.60. Found: C, 30.71; H, 2.36; N, 7.50. Crystals suitable for X-ray diffraction studies were obtained by slow diffusion of *n*-hexane into a solution of **5*cis*** in CH_2Cl_2. When the ratio hexane/CH_2Cl_2 was 5/1, crystals of **5*cis***·0.5(hexane) were isolated, but a smaller ratio led to the crystallization of **5*cis***·CH_2Cl_2.

Synthesis of *trans*-[Pt(κ^2-Aryl)(κ^1-Aryl)(CO)] (5*trans*). Method a. The solid complex **5*cis*** (105 mg, 0.14 mmol) was placed in a flask and heated in a bath at 150 °C with stirring. This temperature was maintained until the resulting liquid solidified to a red solid that was cooled to room temperature. CH_2Cl_2 (4 mL) was added, and the suspension was filtered through Celite. The filtrate was concentrated (1 mL), *n*-pentane (15 mL) was added, and the resulting suspension was filtered off. The solid was washed with *n*-pentane and air-dried to give **5*trans*** as a red solid. Yield: 96 mg, 93%.

Method b. A solution of **5*cis*** (76 mg, 0.10 mmol) in toluene (15 mL) was refluxed for 1 h. After 12 h at room temperature the

solution was evaporated to dryness, the solid was extracted with CH_2Cl_2 (2 mL), and the mixture was filtered through Celite and $MgSO_4$. *n*-Hexane (8 mL) was added to the filtrate, and the suspension was filtered and the solid washed with *n*-hexane and air-dried to give **5*trans*** as a red solid. Yield: 45 mg. 61%. Mp: 172−174 °C. IR (cm^{-1}): ν(C≡O) 2106. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.10 (s, 12 H, OMe), 3.91 (s, 6 H, OMe). $^{13}C\{^1H\}$ NMR (100.81 MHz, $CDCl_3$, 25 °C): δ 154.06 (CO, $^1J_{PtC}$ = 2120 Hz), 152.53 (C Aryl, J_{PtC} = 34 Hz), 144.58 (C Aryl), 143.55 (C Aryl), 134.85 (*i*-C Aryl, $^1J_{PtC}$ = 680 Hz), 62.45 (*m*-OMe), 61.56 (*p*-OMe). Anal. Calcd for $C_{19}H_{18}N_4O_{15}Pt$: C, 30.95; H, 2.46; N, 7.60. Found: C, 30.75; H, 2.16; N, 7.64.

Synthesis of *cis*-[Pt(κ^1-Aryl)$_2$(CO)(PPh$_3$)] (6*cis*). To a stirred solution of **5*cis*** (56 mg, 0.08 mmol) in CH_2Cl_2 (3 mL) was added PPh_3 (20 mg, 0.08 mmol). The resulting yellow solution was concentrated to dryness, Et_2O (2 mL) was added, and the suspension was filtered off. The solid was washed with Et_2O and air-dried to give **6*cis*** as a pale yellow solid. Yield: 63 mg, 83%. Mp: 262−264 °C. IR (cm^{-1}): ν(C≡O) 2100. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60−7.27 (m, 15 H, PPh_3), 3.94 (s, 6 H, OMe), 3.90 (s, 3 H, OMe), 3.77 (s, 6 H, OMe), 3.74 (s, 3 H, OMe). $^{31}P\{^1H\}$ NMR (121.50 MHz, $CDCl_3$): δ 14.05 (s, PPh_3, $^1J_{PtP}$ = 2262 Hz). $^{13}C\{^1H\}$ NMR (75.45 MHz, $CDCl_3$, 25 °C): δ 170.86 (d, CO, $^2J_{PC}$ = 9 Hz, $^1J_{PtC}$ = 1192 Hz), 150.06 (d, *m*-C Aryl trans CO, $^4J_{PC}$ = 2 Hz, $^3J_{PtC}$ = 56 Hz), 148.016 (d, *m*-C Aryl trans PPh_3, $^4J_{PC}$ = 6.6 Hz, $^3J_{PtC}$ = 51 Hz), 148.023 (d, C Aryl, J_{PC} = 2.2 Hz), 144.79 (d, C Aryl, J_{PC} = 2.2 Hz), 144.61 (C Aryl, J_{PtC} = 10 Hz), 144.39 (d, C Aryl, J_{PC} = 1.7 Hz, J_{PtC} = 11 Hz), 134.43 (br, *o*-C PPh_3), 133.36 (d, *i*-C Aryl trans CO, $^2J_{PC}$ = 11 Hz), 131.41 (*p*-C PPh_3), 129.05 (C), 128.49 (d, *m*-C PPh_3, $^3J_{PC}$ = 9.4 Hz), 121.86 (d, *i*-C Aryl trans PPh_3, $^2J_{PC}$ = 104 Hz), 62.34 (*m*-OMe), 62.05 (*m*-OMe), 61.11 (*p*-OMe), 61.03 (*p*-OMe). Anal. Calcd for $C_{37}H_{33}N_4O_{15}PPt$: C, 44.45; H, 3.33; N, 5.60. Found: C, 44.40; H, 3.42; N, 5.53. Single crystals of **6*cis*** were obtained by slow diffusion of Et_2O into a $CDCl_3$ solution of **6*cis***.

Synthesis of *trans*-[Pt(κ^1-Aryl)$_2$(CO)(PPh$_3$)] (6*trans*). To a stirred solution of **5*trans*** (40 mg, 0.05 mmol) in CH_2Cl_2 (2 mL) was added PPh_3 (14 mg, 0.05 mmol). The solution was concentrated (1 mL), and Et_2O (15 mL) was added to give a suspension, which was filtered off. The resulting solid was washed with Et_2O and air-dried to give **6*trans*** as a pale yellow solid. Yield: 30 mg, 55%. Mp: 248−250 °C. IR (cm^{-1}): ν(C≡O) 2122, 2114. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40−7.25 (m, 15 H, PPh_3), 3.80 (s, 6 H, OMe), 3.78 (s, 12 H, OMe). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 5.75 (s, PPh_3, $^1J_{PtP}$ = 3263 Hz). $^{13}C\{^1H\}$ NMR (100.81 MHz, $CDCl_3$, 25 °C): δ 168.29 (d, CO, $^2J_{PC}$ = 150 Hz), 148.62 (*m*-C Aryl, $^3J_{PtC}$ = 39 Hz), 147.53 (*o*-C Aryl, $^2J_{PtC}$ = 15 Hz), 144.19 (*p*-C Aryl), 133.92 (d, *o*-C PPh_3, $^2J_{PC}$ = 10 Hz, $^3J_{PtC}$ = 18 Hz), 130.89 (*p*-C PPh_3, $^4J_{PC}$ = 2.2 Hz), 128.16 (d, *m*-C PPh_3, $^3J_{PC}$ = 11 Hz), 127.55 (d, *i*-C Aryl, $^2J_{PC}$ = 10 Hz), 127.16 (d, *i*-C PPh_3, $^1J_{PC}$ = 61 Hz), 61.97 (*m*-OMe), 61.07 (*p*-OMe). Anal. Calcd for $C_{37}H_{33}N_4O_{15}PPt$: C, 44.18; H, 3.55; N, 5.46. Found: C, 44.45; H, 3.33; N, 5.60. Single crystals of **6*trans***·$CHCl_3$ were obtained by slow diffusion of *n*-hexane into a $CDCl_3$ solution of **6*trans***.

Synthesis of *cis*-[Pt(κ^2-Aryl)(κ^1-Aryl)(PPh$_3$)] (7*cis*). To a solution of *cis*-(Me_4N)[Pt(κ^2-Aryl)(κ^1-Aryl)Cl] (220 mg, 0.27 mmol) in CH_2Cl_2 (4 mL) was added PPh_3 (70 mg, 0.27 mmol). The orange solution was concentrated (1 mL), and Et_2O (15 mL) was added. The resulting suspension was filtered off, and the solid was washed with Et_2O and air-dried to give **7*cis*** as an orange solid. Yield: 250 mg, 96%. Mp: 305−309 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43−7.32 (m, 15 H, PPh_3), 4.03 (s, 3 H, OMe), 4.00 (s, 3 H, OMe), 3.852 (s, 3 H, OMe), 3.848 (s, 6 H, OMe), 3.81 (s, 3 H, OMe). $^{31}P\{^1H\}$ NMR (121.50 MHz, $CDCl_3$): δ 16.53 (s, $^1J_{PtP}$ = 2579 Hz). $^{13}C\{^1H\}$ NMR (75.45 MHz, $CDCl_3$): δ 154.25 (d, *m*-C κ^2-Aryl, $^4J_{PC}$ = 8 Hz), 154.17 (d, *m*-C κ^2-Aryl, $^4J_{PC}$ = 12 Hz), 148.36 (d, *m*-C κ^1-Aryl, $^4J_{PC}$ = 2 Hz, $^3J_{PtC}$ = 76 Hz), 146.98 (*o*-C Aryl), 146.29 (d, *o*-C Aryl, $^3J_{PC}$ = 2.6 Hz), 143.84 (*p*-C k^1-Aryl), 143.32 (d, *p*-C κ^2-Aryl, $^5J_{PC}$ = 2 Hz), 141.30 (d, *i*-C κ^2-Aryl, $^1J_{PC}$ = 109 Hz), 137.31 (d, *o*-C κ^2-Aryl, J_{PC} = 5 Hz), 134.25 (d, *o*-C PPh_3, $^2J_{PC}$ = 10 Hz), 130.80 (*p*-C PPh_3), 129.00 (d, *i*-C PPh_3, $^1J_{PC}$ = 52 Hz), 128.26 (d, *m*-C PPh_3, $^3J_{PC}$ = 11 Hz), 114.68 (d, *i*-C κ^1-Aryl, $^2J_{PC}$ = 12 Hz), 62.25 (OMe), 62.01 (2 OMe), 61.95 (OMe), 61.38 (2 OMe). Anal. Calcd for $C_{36}H_{33}N_4O_{14}PPt$: C, 44.50; H, 3.42; N, 5.77. Found: C, 44.44; H, 3.35; N, 5.68. Single crystals of **7*cis***·Me_2CO were obtained by slow diffusion of Et_2O or *n*-hexane into a solution of **4*cis*** in acetone.

Synthesis of *cis*-[Pt(κ^1-Aryl)$_2$(PPh$_3$)$_2$] (8*cis*). To a solution of *cis*-(Me_4N)[Pt(κ^2-Aryl)(κ^1-Aryl)Cl] (116 mg, 0.14 mmol) in CH_2Cl_2 (5 mL) was added PPh_3 (149 mg, 0.57 mmol). The resulting suspension was filtered, the filtrate was concentrated (1 mL), and Et_2O (15 mL) was added. The suspension was filtered off and the solid was washed with Et_2O and air-dried to give **8*cis*** as a yellow solid. Yield: 152 mg, 87%. Mp: 130−132 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.71−6.96 (m, 30 H, PPh_3), 4.028 (s, 3 H, OMe), 3.996 (s, 3 H, OMe), 3.849 (s, 3 H, OMe), 3.846 (s, 6 H, OMe), 3.805 (s, 3 H, OMe), 3.754 (s, 6 H, OMe), 3.750 (s, 12 H, OMe). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 16.53 (s, $^1J_{PtP}$ = 2579 Hz), 6.50 (s, $^1J_{PtP}$ = 2369 Hz), −4.61 (s, PPh_3). Anal. Calcd for $C_{54}H_{48}N_4O_{14}P_2Pt$: C, 52.56; H, 3.92; N, 4.5. Found: C, 52.34; H, 4.19; N, 4.46.

Synthesis of *trans*-[Pt(κ^1-Aryl)$_2$(PPh$_3$)$_2$] (8*trans*). A solution of **6*trans*** (65 mg, 0.09 mmol) in CH_2Cl_2 (5 mL) was stirred for 7 h with PPh_3 (47 mg, 0.18 mmol) under N_2. The resulting solution was filtered through Celite, the filtrate was concentrated (2 mL), and Et_2O (15 mL) was added. The suspension was filtered off and the solid washed with Et_2O and air-dried to give **8*trans*** as a yellow solid. The filtrate was concentrated to dryness, the residue was extracted with Et_2O (15 mL), and the suspension was filtered off to give a second crop of **8*trans***. Yield: 90 mg, 83%. Mp: 163−164 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.57−7.51 (m, 12 H, PPh_3), 7.25−7.17 (m, 18 H, PPh_3), 3.61 (s, 6 H, OMe), 3.52 (s, 12 H, OMe). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 8.33 (s, $^1J_{PtP}$ = 2890 Hz). $^{13}C\{^1H\}$ NMR (75.45 MHz, $CDCl_3$): δ 148.15 (t, *m*-C Aryl, $^4J_{PC}$ = 1 Hz, $^3J_{PtC}$ = 41 Hz), 146.68 (t, *o*-C Aryl, $^3J_{PC}$ = 2 Hz, $^3J_{PtC}$ = 19 Hz), 142.73 (*p*-C Aryl, J_{PtC} = 1 Hz), 137.36 (t, *i*-C Aryl, $^2J_{PC}$ = 11 Hz), 134.70 (vt, *o*-C PPh_3, $|^2J_{PC} + {}^4J_{PC}|$ = 6 Hz), 131.07 (vt, *i*-C PPh_3, $|^1J_{PC} + {}^3J_{PC}|$ = 28 Hz), 129.64 (*p*-C PPh_3), 127.05 (vt, *m*-C PPh_3, $|^3J_{PC} + {}^5J_{PC}|$ = 5 Hz), 61.65 (*m*-OMe), 60.94 (*p*-OMe). Anal. Calcd for $C_{54}H_{48}N_4O_{14}P_2Pt$: C, 52.56; H, 3.92; N, 4.50. Found: C, 52.62; H, 3.93; N, 4.52. Single crystals of **8*trans***·$0.5CHCl_3$ were obtained by slow diffusion of *n*-hexane into a solution of **8*trans*** in $CHCl_3$.

X-ray Structure Determinations. Numerical details are presented in Table 1. Data were recorded at low temperature on a Bruker SMART 1000 CCD diffractometer using Mo Kα radiation. Absorption corrections were based on indexed faces (**2*cis*, 3*trans*, 7*cis***) or multiple scans (all other structures; program SADABS). Structures were refined anisotropically on F^2 using the program SHELXL-97 (Prof. G. M. Sheldrick, University of Göttingen). Restraints to light atom displacement factors and local ring symmetry were employed to improve the stability of refinement. Hydrogen atoms were refined using a riding model or rigid methyl groups. Special features of the refinements are as follows. **3*cis***: the chloroform molecule is disordered over two positions, as is the methyl group C17. **4*trans***: the extremely large cell led to a weak diffraction pattern. An extensive system of restraints was used. Only two molecules per block could be refined simultaneously. Four areas of poorly defined electron density were tentatively identified as disordered solvent (chloroform), but no suitable refinement model was found. The program SQUEEZE[26] was therefore used to mathematically remove the effects of the solvent. Methyl H atoms

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Table 1. Crystallographic Data for the Complexes 2*cis*, 3*cis*·$CHCl_3$, 3*trans*, 4*trans*·$CHCl_3$, 5*cis*·CH_2Cl_2, 5*cis*·0.5(hexane), 6*cis*, 6*trans*·$CHCl_3$, 7*cis*·Me_2CO, and 8*trans*·0.5$CHCl_3$

	2*cis*	**3*cis*·$CHCl_3$**	**3*trans***	**4*trans*·$CHCl_3$**	**5*cis*·CH_2Cl_2**
formula	$C_{20}H_{24}N_4O_{15}PtS$	$C_{37}H_{37}Cl_3N_6O_{14}Pt$	$C_{36}H_{36}N_6O_{14}Pt$	$C_{28}H_{28}Cl_3N_5O_{14}Pt$	$C_{20}H_{20}Cl_2N_4O_{15}Pt$
M_r	787.58	1091.17	971.80	959.99	822.39
cryst habit	orange tablet	pale yellow tablet	pale yellow lath	orange prism	orange lath
cryst size (mm)	0.22 × 0.19 × 0.09	0.38 × 0.28 × 0.16	0.38 × 0.10 × 0.03	0.30 × 0.12 × 0.08	0.41 × 0.11 × 0.05
cryst syst	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2/n$	$P2_1/n$
cell constants					
a, Å	9.3407(8)	9.9644(15)	21.1834(16)	32.917(3)	10.5115(8)
b, Å	34.741(3)	13.156(2)	11.2289(8)	8.5440(8)	9.5613(6)
c, Å	8.6000(6)	17.352(3)	16.2941(12)	51.357(5)	26.9995(18)
α, deg	90	84.802(3)	90	90	90
β, deg	103.794(4)	74.979(3)	93.091(2)	104.698(8)	92.123(3)
γ, deg	90	85.990(3)	90	90	90
V (Å^3)	2710.3	2185.4	3870.2	13971	2711.7
Z	4	2	4	16	4
λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
ρ(calcd) (Mg m^{-3})	1.930	1.658	1.668	1.826	2.014
μ (mm^{-1})	5.33	3.46	3.70	4.32	5.45
F(000)	1544	1084	1936	7552	1600
T (K)	143	143	143	133	143
$2\theta_{max}$ (deg)	61	60	60	52.6	60
no. of rflns measd	59 825	36 041	82 134	164 110	42 013
no. of indep rflns	8272	12 710	11 308	28 569	7934
transmissions	0.28−0.60	0.51−0.75	0.30−0.87	0.40−0.75	0.52−0.93
R_{int}	0.045	0.045	0.073	0.136	0.047
no. of restraints/params	86/378	627/606	148/524	3554/1701	36/380
$R_w(F^2$, all rflns)	0.0523	0.0635	0.0554	0.184	0.0680
$R(F, > 4\sigma(F))$	0.0263	0.0274	0.0255	0.073	0.0285
S	1.23	1.03	1.00	0.99	1.09
max $\Delta\rho$ (e Å^{-3})	1.3	1.5	1.9	3.2	2.7

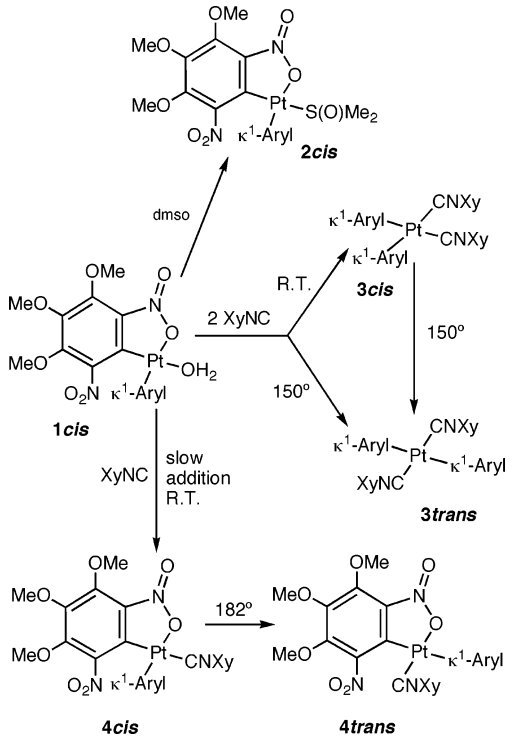
	5*cis*·0.5(hexane)	**6*cis***	**6*trans*·$CHCl_3$**	**7*cis*·Me_2CO**	**8*trans*·0.5$CHCl_3$**
formula	$C_{22}H_{25}N_4O_{15}Pt$	$C_{37}H_{33}N_4O_{15}Pt$	$C_{38}H_{34}Cl_3N_4O_{15}Pt$	$C_{39}H_{39}N_4O_{15}Pt$	$C_{54.5}H_{48.5}Cl_{1.5}N_4O_{14}P_2Pt$
M_r	780.55	999.73	1119.10	1029.80	1293.68
cryst habit	red prism	pale yellow tablet	amber tablet	red tablet	yellow prism
cryst size (mm)	0.29 × 0.14 × 0.12	0.38 × 0.30 × 0.15	0.36 × 0.15 × 0.06	0.28 × 0.20 × 0.08	0.22 × 0.17 × 0.13
cryst syst	triclinic	orthorhombic	monoclinic	monoclinic	triclinic
space group	$P\bar{1}$	*Pbca*	$P2_1/n$	$P2_1/n$	$P\bar{1}$
cell constants					
a, Å	9.0734(6)	18.1068(11)	9.9072(8)	20.9579(14)	12.2189(8)
b, Å	10.5091(8)	20.7282(13)	40.753(3)	9.4999(6)	13.1105(10)
c, Å	15.3912(11)	20.7627(13)	10.6809(8)	22.4791(16)	18.8240(14)
α, deg	72.588(3)	90	90	90	88.649(4)
β, deg	88.431(3)	90	103.874(3)	115.389(3)	76.049(4)
γ, deg	83.900(3)	90	90	90	63.967(4)
V (Å^3)	1392.4	7792.7	4186.8	4043.3	2617.9
Z	2	8	4	4	2
λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
ρ(calcd) (Mg m−^{3})	1.862	1.704	1.775	1.692	1.641
μ (mm^{-1})	5.12	3.72	3.66	3.59	2.89
F(000)	766	3968	2216	2056	1298
T (K)	133	133	133	143	133
$2\theta_{max}$ (deg)	60	60	60	60	61
no. of rflns measd	32 640	127 547	76 053	84 387	53 092
no. of indep rflns	8134	11 404	10 391	11 837	15 887
transmissions	0.47−0.70	0.52−0.75	0.58−0.83	0.41−0.76	0.59−0.71
R_{int}	0.027	0.028	0.050	0.060	0.038
no. of restraints/params	39/385	84/529	72/565	99/549	6/713
$R_w(F^2$, all rflns)	0.0430	0.0495	0.0897	0.0529	0.0298
$R(F, > 4\sigma(F))$	0.0172	0.0191	0.0436	0.0228	0.0686
S	1.00	1.03	1.23	0.99	1.06
max $\Delta\rho$ (e Å^{-3})	1.6	1.4	1.9	1.1	1.6

of the isonitrile ligands were indistinct. Esd's of molecular dimensions are appreciably larger than for all other structures reported here. **7*cis***: solvent H atoms are indistinct. **8*trans***: the chloroform molecule is disordered over an inversion center. CCDC-600162 (**2*cis***), CCDC-600163 (**3*cis***·$CHCl_3$), CCDC-600164 (**3*trans***), CCDC-600165 (**4*trans***·$CHCl_3$), CCDC-600166 (**5*cis***·CH_2Cl_2), CCDC-600167 (**5*cis***·0.5hexane), CCDC-600168 (**6*cis***), CCDC-600169 (**6*trans***·$CHCl_3$), CCDC-600170 (**7*cis***·Me_2CO), and CCDC-600171 (**8*trans***·0.5$CHCl_3$) contain supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

Reactivity of *cis*-[Pt(κ^2-Aryl)(κ^1-Aryl)(OH_2)] (1*cis*) toward dmso and XyNC. Synthesis of *cis*- and *trans*-[Pt(κ^1-Aryl)$_2$-(CNXy)$_2$] and *cis*- and *trans*-[Pt(κ^2-Aryl)(κ^1-Aryl)(CNXy)]. The addition of dmso to a CH_2Cl_2 or Et_2O solution of complex **1*cis*** (1:1 or 1:2 molar ratio) gave *cis*-[Pt(κ^2-Aryl)(κ^1-Aryl)(*S*-

Scheme 1. Synthesis of Complexes 3 and 4



dmso)] (**2*cis***; Scheme 1). The reaction (1:1 or 1:2 molar ratio) was followed in d_6-acetone by 1H NMR spectroscopy, and the only platinum complex observed in solution was **2*cis*.**

The room-temperature reaction of **1*cis*** with XyNC (1:2; Xy = 2,6-$Me_2C_6H_4$) in CH_2Cl_2 gives almost instantly *cis*-[Pt(κ^1-Aryl)$_2$(CNXy)$_2$] (**3*cis***; Scheme 1). When the same mixture of reagents was refluxed in toluene for 5 h, a mixture of **3*cis*** and **3*trans*** (approximately 1:1.2) was isolated. The pure complex *trans*-[Pt(κ^1-Aryl)$_2$(CNXy)$_2$] (**3*trans***) can be obtained by heating a mixture of **1*cis*** and XyNC (1:2) at 150 °C in a Carius tube or **3*cis*** in toluene for 75 min. An excess of XyNC catalyzes this isomerization process. Thus, heating a toluene solution of **3*cis*** (45 mg in 10 mL) at 150 °C in a Carius tube gave after 1 h only a 25:1 mixture of **3*cis*** and **3*trans***, while the same experiment in the presence of 10 equiv of XyNC gave a 1:1 mixture. The isomerization is favored in the presence of added XyNC because it assists the formation of the required five-coordinate transition state.[27] The mechanism for the thermal isomerization without addition of XyNC (and also for that of the others reported below) can imply the formation of a high-energy five-coordinate intermediate involving a κ^2-Aryl ligand or the dissociation of XyNC.[28]

When the reaction between **1*cis*** and XyNC was attempted at room temperature in a 1:1 molar ratio, equimolecular amounts of **1*cis*** and **3*cis*** were obtained, instead of the expected complex *cis*-[Pt(κ^2-Aryl)(κ^1-Aryl)(CNXy)] (**4*cis***). For the synthesis of **4*cis***, it is necessary to slowly add a CH_2Cl_2 solution of XyNC to a CH_2Cl_2 solution of **1*cis***, in a 1:1 molar ratio. Therefore, complex **4*cis*** is an intermediate in the process of formation of **3*cis*** from **1*cis***, the second step being faster than the first. Melting of the complex **4*cis*** (181−182 °C) led to its isomer **4*trans*** (Scheme 1).

Reactions of 1*cis* with CO. Synthesis of *cis*- and *trans*-[Pt(κ^2-Aryl)(κ^1-Aryl)(CO)]. By bubbling CO through a red CH_2Cl_2 or acetone solution of complex **1*cis*** for 5 min at room temperature, the yellow complex *cis*-[Pt(κ^2-Aryl)(κ^1-Aryl)(CO)] (**5*cis***) was obtained (Scheme 2). The reaction between the red *cis*-[Pt(κ^2-(*C*,*O*)-$C_6H_4NO_2$)$_2$] and excess CO was also reported to give a yellow solution, but attempts to isolate the expected carbonyl complex, probably formed in solution, gave the starting material.[29]

The complex **5*cis*** is stable in CH_2Cl_2, acetone, toluene, and $CHCl_3$ solutions and also in the solid state at room temperature; it decomposes on melting (160 °C) to give *trans*-[Pt(κ^2-Aryl)(κ^1-Aryl)(CO)] (**5*trans***). The complex **5*trans*** could also be obtained by heating a solution of **5*cis*** (1 h refluxing in toluene or at 150 °C in a Carius tube), but the yields (61 or 51%, respectively) were smaller than that of the fusion method (93%). In this case, the mechanism must be the one proposed above for the isomerization of **3*cis*** or **4*cis*** involving the formation of a five-coordinate intermediate through a κ^1-Aryl → κ^2-Aryl transformation, because the other, involving the dissociation of the neutral ligand, would in this case lead to decomposition instead of isomerization.

In an attempt to prepare a complex containing Pt−Hg bonds, similar to those that we reported previously,[24] we reacted **5*cis*** at room temperature with $Hg(OAc)_2$ in a 2:1 molar ratio but, surprisingly, we isolated complex **5*trans*** and observed the formation of mercury. It is likely that the isomerization process occurs through an unstable Pt−Hg intermediate that decomposes to give Hg, some coupling product, and **5*trans***.

Reactivity of *cis*- and *trans*-[Pt(κ^2-Aryl)(κ^1-Aryl)(CO)] (5). Complexes **5** have been shown to be suitable precursors for the synthesis of *cis*- and *trans*-[Pt(κ^2-Aryl)(κ^1-Aryl)L] complexes (Scheme 3). With this purpose, we chose the neutral ligands XyNC and PPh_3. The room-temperature reactions of complexes **5** with XyNC (1:2) led to the corresponding complexes **3** (Scheme 2). When equimolecular amounts of XyNC and **5** were reacted, mixtures of the corresponding complexes **3**−**5** were identified in solution. However, pure complexes **4** could be isolated from these solutions in moderate yields (approximately 50%) by crystallization.

PPh_3 reacts differently from XyNC with equimolecular amounts of complexes **5**. Thus, instead of replacing CO, PPh_3 coordinates trans to the κ^1-Aryl ligand, replacing the oxygen atom of κ^2-Aryl and giving *cis*-[Pt(κ^1-Aryl)$_2$(CO)(PPh_3)] (**6*cis***) or *trans*-[Pt(κ^1-Aryl)$_2$(CO)(PPh_3)] (**6*trans***) (Scheme 2). All attempts to isomerize complexes **6** by heating were unfruitful, because the complex *cis*-[Pt(κ^2-Aryl)(κ^1-Aryl)(PPh_3)] (**7*cis***) was obtained instead (Scheme 3). This complex results by replacement of the carbonyl ligand by the oxygen atom of a nitro group and, in the case of **6*trans***, after an additional isomerization. Correspondingly, ^{1}H and ^{31}P NMR spectra show that **6*cis*** decomposes in solution at room temperature more quickly than **6*trans***. In addition, the intermediate product of the isomerization process of the latter (probably the product of CO substitution, **7*trans***) was not observed. If **7*trans*** is an intermediate, it is probably highly unstable, and its isomerization very fast, because of the steric hindrance between PPh_3 and the uncoordinated nitro group of the κ^2-Aryl ligand. The analogous **4*trans*** complex is stable because of the smaller spatial demand of the XyNC around the metal center.

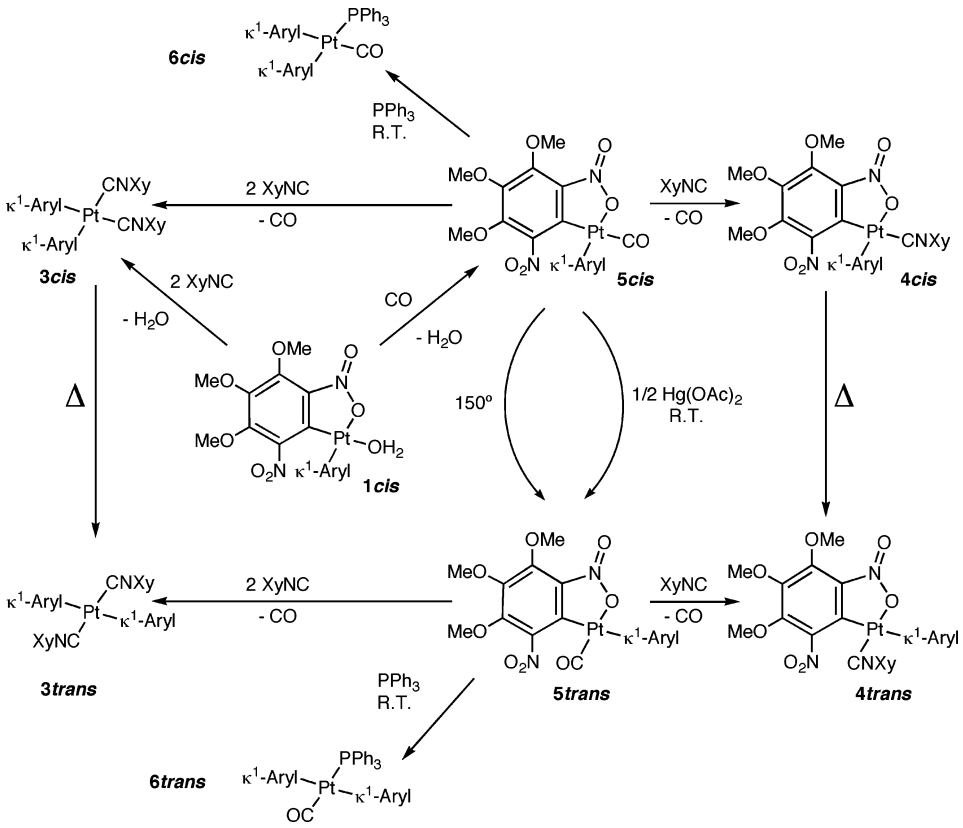
The complex **7*cis*** can be obtained more directly in better yield (96%) by reacting PPh_3 with *cis*-(Me_4N)[Pt(κ^2-Aryl)(κ^1-Aryl)Cl], the starting material for all members of this family of bis(2,6-dinitroaryl)platinum complexes, in a 1:1 molar ratio

(27) Favez, R.; Roulet, R.; Pinkerton, A. A.; Schwarzenbach, D. *Inorg. Chem.* **1980**, *19*, 1356.

(28) Price, J. H.; Birk, J. P.; Wayland, B. B. *Inorg. Chem.* **1978**, *17*, 2245.

(29) Vicente, J.; Chicote, M. T.; Martin, J.; Jones, P. G.; Fittschen, C.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1986**, 2215.

Scheme 2. Synthesis of Complexes 3−6



(Scheme 3). A 1:2 reaction gives a mixture of **7*cis*** and *cis*-[Pt(κ^1-Aryl)$_2$(PPh$_3$)$_2$] (**8*cis***). As the complex **8*cis*** is in solution in equilibrium with **7*cis*** + PPh$_3$ (see Spectroscopic Properties), the isolation of pure **8*cis*** requires an excess of PPh$_3$ (1:4); otherwise, mixtures of **7*cis*** and **8*cis*** are isolated. The complex **8*trans*** can be prepared by the room-temperature reaction of **6*trans*** with PPh$_3$. It is air stable at room temperature, in the solid state, and, in contrast to the case for **8*cis***, in solution (see below).

In contrast to **3*cis*−5*cis***, PPh$_3$ complexes **6**−**8** do not isomerize when they are heated for 1 h at 150 °C in a Carius tube. Instead, complexes **6*cis*** and **6*trans*** give **7*cis***, even in solution at room temperature, **7*cis*** remains unaltered, and **8*cis*** and **8*trans*** give **7*cis*** and OPPh$_3$ when they melt. This thermal decomposition of **8*trans*** can occur after isomerization to **8*cis*** and decomposition to **7*cis*** or, as we have suggested above for the decomposition of **6*trans*,** through the intermediacy of **7*trans*.** We also believe that this second reaction pathway is more reasonable because all thermally stable [Pt(aryl)$_2$(PPh$_3$)$_2$] complexes are trans.[14−16]

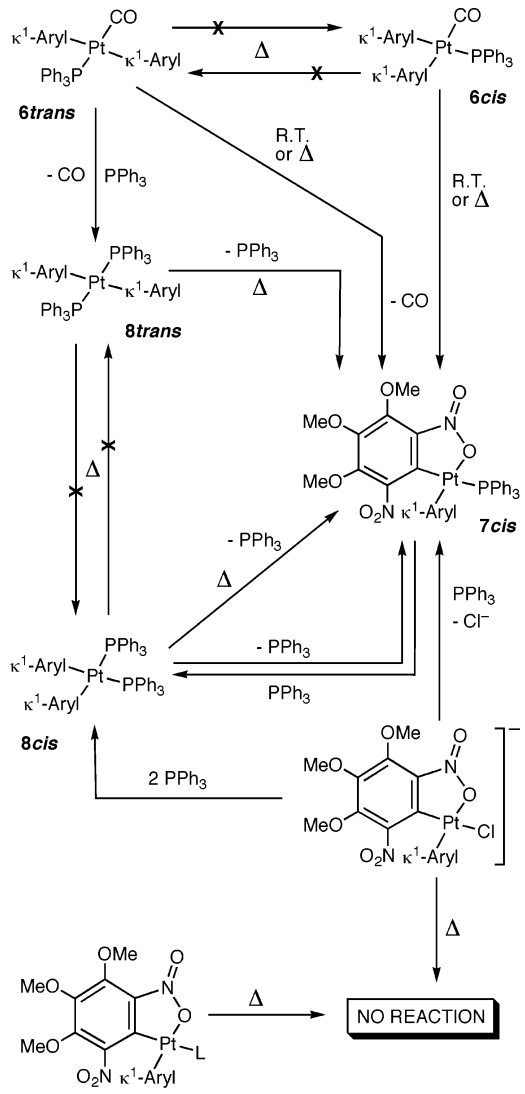
Attempts to isomerize *cis*-[Pt(κ^2-Aryl)(κ^1-Aryl)L] (L = H$_2$O (**1*cis***), PhCN, tht,[22] *S*-dmso (**2*cis***)) by heating a toluene solution for 1 h at 150 °C in a Carius tube or heating at the melting point were unsuccessful. The complex **1*cis*** gave a mixture of unidentified products, and the others were recovered unchanged.

Conclusions on the Cis/Trans Isomerization Reactions. The cis to trans thermal isomerization occurs for *cis*-[Pt(κ^2-Aryl)(κ^1-Aryl)L] when L is the carbon donor ligand CO or XyNC but not when L is an N, S, or O donor or for *cis*-[Pt(κ^2-Aryl)(κ^1-Aryl)Cl]$^-$. A reasonable explanation for this behavior is that because the carbon donor ligands display a similar transphobia (see refs 30 and 31), i.e. *T*[Aryl/Aryl] ≈ *T*[Aryl/CNR] ≈ *T*[Aryl/CO], the trans isomers are preferred on steric grounds. There have been no other [M(κ^2-aryl)(κ^1-aryl)L] (M = Pd, Pt; L = CO, RNC) complexes characterized by X-ray diffraction studies,[11] but it would be interesting to study the stability of related complexes as a function of the nature of L and the steric requirements of the ligands. The fact that some cis complexes resist high temperatures without isomerization means that repulsions between the diaryl ligands are not important enough to compensate for transphobia effects because *T*[Aryl/Aryl] ≫ *T*[Aryl/L(N,S,O,Cl)] (L(N,S,O) = ligand with N, S, or O donor atoms, e.g. PhCN, tht, *S*-dmso, O-bonded nitro group, Cl$^-$). All the known group 10 metal complexes [M(aryl)$_2$-

(30) Vicente, J.; Arcas, A.; Bautista, D.; Jones, P. G. *Organometallics* **1997**, *16*, 2127. Vicente, J.; Abad, J. A.; Frankland, A. D.; Ramírez de Arellano, M. C. *Chem. Eur. J.* **1999**, *5*, 3066. Vicente, J.; Arcas, A.; Bautista, D.; Ramírez de Arellano, M. C. *J. Organomet. Chem.* **2002**, *663*, 164. Vicente, J.; Abad, J. A.; Martínez-Viviente, E.; Jones, P. G. *Organometallics* **2002**, *21*, 4454.

(31) Albert, J.; Cadena, J. M.; Delgado, S.; Granell, J. *J. Organomet. Chem.* **2000**, *603*, 235. Albert, J.; Cadena, J. M.; Granell, J. R.; Solans, X.; Font Bardia, M. *Tetrahedron: Asymmetry* **2000**, *11*, 1943. Albert, J.; Bosque, R.; Cadena, J. M.; Granell, J. R.; Muller, G.; Ordinas, J. I. *Tetrahedron: Asymmetry* **2000**, *11*, 3335. Albert, J.; Bosque, R.; Cadena, J. M.; Delgado, S.; Granell, J. *J. Organomet. Chem.* **2001**, *634*, 83. Amatore, C.; Bahsoun, A. A.; Jutand, A.; Meyer, G.; Ntepe, A. N.; Ricard, L. *J. Am. Chem. Soc.* **2003**, *125*, 4212. Bartolome, C.; Espinet, P.; Vicente, L.; Villafañe, F.; Charmant, J. P. H.; Orpen, A. G. *Organometallics* **2002**, *21*, 3536. Carbayo, A.; Cuevas, J. Y.; Garcia Herbosa, G.; Garcia Granda, S.; Miguel, D. *Eur. J. Inorg. Chem.* **2001**, 2361. Carbayo, A.; Cuevas, J. V.; Garcia Herbosa, G. *J. Organomet. Chem.* **2002**, *658*, 15. Crespo, M.; Granell, J.; Solans, X.; Font-Bardía, M. *J. Organomet. Chem.* **2003**, *681*, 143. Fernandez, S.; Navarro, R.; Urriolabeitia, E. P. *J. Organomet. Chem.* **2000**, *602*, 151. Fernandez, A.; Vazquez Garcia, D.; Fernandez, J. J.; López Torres, M.; Suarez, A.; Castro Juiz, S.; Vila, J. M. *Eur. J. Inorg. Chem.* **2002**, 2389. Fernandez-Rivas, C.; Cardenas, D. J.; Martin-Matute, B.; Monge, A.; Gutierrez-Puebla, E.; Echavarren, A. M. *Organometallics* **2001**, *20*, 2998. Jalil, M. A.; Fujinami, S.; Nishikawa, H. *Dalton Trans.* **2001**, 1091. Larraz, C.; Navarro, R.; Urriolabeitia, E. P. *New J. Chem.* **2000**, *24*, 623. Lohner, P.; Pfeffer, M.; Fischer, J. *J. Organomet. Chem.* **2000**, *607*, 12. López, C.; Caubet, A.; Pérez, S.; Solans, X.; Font-Bardía, M. *J. Organomet. Chem.* **2003**, *681*, 82. Marshall, W. J.; Grushin, V. V. *Organometallics* **2003**, *22*, 555.

Scheme 3. Synthesis of Complexes 7 and 8



(CO)L] (aryl = C_6F_5,[8,9,32,33] Ph;[34] M = Ni,[33] Pt[8,9,32,34]) characterized by X-ray diffraction studies are of cis geometry, unless the nature of some ligand forces a trans geometry. However, they were all prepared from cis complexes and isolated at room or lower temperatures. In agreement with our results, the thermal treatment of some of these C_6F_5 or related 2,6-disubstituted aryl complexes could give their trans isomers. Indeed, it has recently been reported that heating a benzene or cyclohexane solution of *cis*-[Pt(C_6F_5)$_2$(CO)(tht)] at 50−60 °C for 1 h results in the formation of the corresponding trans isomer.[9]

The thermal isomerization of **3*cis*** to **3*trans*** also agrees with the greater stability of the trans isomers on steric grounds. There has only been one platinum complex of the type *trans*-[Pt$_3$(aryl)$_6$-{(CN)$_2$R}$_3$] characterized by X-ray diffraction studies, where aryl = C_6F_5, R = C_6H_4-1,2, but it was obtained at room temperature from *trans*-[Pt(C_6F_5)$_2$($AsPh_3$)$_2$].[35] The only reported [M(κ^1-aryl)$_2$(CNR)$_2$] complexes characterized by X-ray diffraction (M = group 10 elements) are those with M = Ni, aryl = C_6F_5, R = ^{t}Bu[33] and M = Pd, aryl = $C_6H_2(CF_3)_3$-2,4,6, R = C_6H_5Me-4,[36] and these are also trans. Supporting the greater thermodynamic stabilility of these trans isomers is the fact that the Ni complex is obtained from *cis*-[Ni(κ^1-aryl)$_2$L$_2$] (L = CO, thf) at room temperature. Although in solution a mixture of the cis and trans isomers is formed, the isolated and stable species in the solid state is the trans isomer. The more stable members of the family of diaryl complexes [Pd(R)$_2$(L)(L′)] (R = C_6H_2-$(CF_3)_3$-2,4,6) and L = MeCN, L′ = Me_2S, tht; L = L′ = 4-picoline) and [Pd(κ^1-aryl)$_2$X(L)]$^-$ (L = Me_2S, tht, X = I)[36] are also of trans geometry, despite the expected electronic preferences (T[Aryl/Aryl] > T[Aryl/L(N,S,I)]), which means that the crowding associated with these two cis ligands is much more important than in our complexes. The same can be assumed about the great stability of complexes *trans*-[Pt(R)-(R′)L$_2$] (R = R′ = 2,3,4,5,6-pentamethylphenyl, 2,4,6-trimethylphenyl, 2,6-dimethylphenyl and L = *S*-dmso, PEt_3[3,4] or R = R′ = $C_6H_4CF_3$-4,[13] 2,6-$Me_2C_6H_3$, 2,4,6-$Me_3C_6H_2$,[4] (L = PEt_3), 2,4,6-$(MeO)_3C_6H_2$,[14] 3,5-$(CF_3)_2C_6H_3$,[15] Ph[16] (L = PPh_3); R = Ph, α-biphenylenyl, R′ = α-biphenyl (R = PEt_3)) and [Pt(2,2′-tetraphenyl)(PEt_3)$_2$]).[17] The large T[Aryl/PR_3] values of those complexes with L = PR_3, and the steric demand of the phosphine in those with L = PPh_3, are also in favor of the trans geometry.

The thermal decomposition of the PPh_3 complexes **6** and **8** to give **7*cis*** prevents us from establishing whether the cis isomers are more stable than the trans isomers or not. The formation of **7*cis*** from the cis complexes is favored by the facility of CO and PPh_3 replacement by the oxygen atom of the nitro group, even at room temperature, and by the chelate effect. The nonisomerization of **7*cis*** is probably attributable to the steric hindrance between PPh_3 and the uncoordinated nitro group of the κ^2-Aryl ligand in its isomer **7*trans*** and also to T[Aryl/Aryl] being slightly greater than T[Aryl/PR_3]. The instability of **7*trans*** is probably the reason for the formation of **7*cis*** from **6*trans*** and **8*trans*** because, as mentioned above, **7*trans*** could be the first product of the decomposition of these complexes. These trans to cis isomerizations and those recently reported by van Koten ([Pt(C∧N)$_2$], where C∧N = ortho-substituted (dimethylamino)methylaryl),[2] can be explained as the consequence of T[Aryl/Aryl] > T[Aryl/L] and of the similar (probably in van Koten's case) or greater (our case) interligand repulsions in the trans isomers. The same applies to the other stable *cis*-diarylplatinum(II) complexes,[3,4,18] although those having a P-donor ligand[19−21] are, in agreement with our proposal, on the borderline between the stable cis and trans isomers because T[Aryl/Aryl] is only slightly greater than T[Aryl/PR_3]. In fact, a 5:1 mixture of *cis*- and *trans*-[Pt{κ(*C*,*P*)-C_6H_3($NHPPh_2$)-2-C(O)Me-3}$_2$] is obtained in the thermal cycloplatination of [$PtMe_2${$P(Ph)_2NHC_6H_4C(O)$Me-2}].[19]

We believe that, in view of our results and those of others, the complexes *cis*-[Pt(aryl)$_2$L$_2$] are more stable than the trans isomers if L ligands are N, O, or S donor ligands because T[Aryl/Aryl] ≫ T[Aryl/L(N,O,S)] unless the aryl or L ligands are highly voluminous. However, because T[Aryl/Aryl] is similar to T[Aryl/L(C,P)], the complexes *trans*-[Pt(aryl)$_2${L(C,P)}$_2$] can be more stable than the cis isomers if interligand repulsions

(32) Berenguer, J. R.; Fornies, J.; Lalinde, E.; Martin, A.; Moreno, M. T. *J. Chem. Soc., Dalton Trans.* **1994**, 3343. Casas, J. M.; Fornies, J.; Martinez, F.; Rueda, A. J.; Tomas, M.; Welch, A. J. *Inorg. Chem.* **1999**, *38*, 1529. Falvello, L. R.; Fornies, J.; Fortuno, C.; Martin, A.; Martinez-Sarinena, A. P. *Organometallics* **1997**, *16*, 5849. Usón, R.; Forniés, J.; Usón, M. A.; Yague, J. F.; Jones, P. G.; Meyer-Bäse, K. *J. Chem. Soc., Dalton Trans.* **1986**, 947.

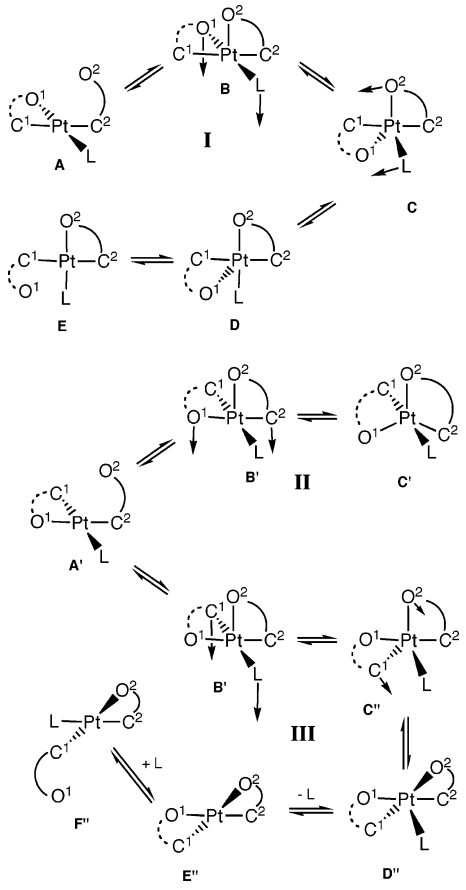
(33) Fornies, J.; Martin, A.; Martin, L. F.; Menjon, B.; Kalamarides, H. A.; Rhodes, L. F.; Day, C. S.; Day, V. W. *Chem. Eur. J.* **2002**, *8*, 4925.

(34) Romeo, R.; Arena, G.; Scolaro, L. M.; Plutino, M. R.; Bruno, G.; Nicolo, F. *Inorg. Chem.* **1994**, *33*, 4029.

(35) Espinet, P.; Soulantica, K.; Charmant, J. P. H.; Orpen, A. G. *Chem. Commun.* **2000**, 915.

(36) Bartolome, C.; Espinet, P.; Martin Alvarez, J. M.; Villafañe, F. *Eur. J. Inorg. Chem.* **2004**, 2326.

Scheme 4. Proposed Pseudorotation Processes To Explain the κ^2-Aryl ⇆ κ^1-Aryl Exchange in *trans*- and *cis*-Diarylplatinum(II) Complexes



are important. Therefore, the complexes *cis*-[Pt(aryl)$_2$L$_2$] containing C (CO, isocyanides, etc.) or P donor ligands could isomerize to their trans isomers by heating if the temperature required for such isomerization is below their decomposition temperatures and the ligands are sufficiently bulky.

Spectroscopic Properties. At room temperature, the ^{1}H and ^{13}C NMR spectra of complexes show the expected three (1:1:1) or two (2:1) MeO singlets per κ^2-Aryl or κ^1-Aryl groups, respectively, except in those of **8*cis***, which shows the equilibrium **8*cis*** ⇄ **7*cis*** + PPh_3 (see below) and **4*trans*** and **5*trans***, which show only two MeO resonances (2:1), instead of five, because both aryl ligands are rapidly exchanging their roles: κ^2-Aryl ⇄ κ^1-Aryl. This process can be slowed enough at −60 °C in **4*trans*** to see the expected five resonances in its ^{1}H NMR spectrum, but in **5*trans*** even at −90 °C only two broad signals were observed. To explain why this exchange occurs in **4*trans*** and **5*trans*** and not in the corresponding **4*cis*** and **5*cis***, we propose the pseudorotation processes shown in Scheme 4. The first step in these fluxional processes should transform the starting complex **A** (route **I** for the trans complexes) or **A′** (route **II** for the cis complexes) into the square-pyramidal structure **B** or **B′**, respectively, after coordination of O^2. One way to achieve the structure resulting after the κ^2-Aryl ⇆ κ^1-Aryl exchange (**E** in route **I** or **F″** in route **III**) is to transform **B** or **B′** into a structure in which O^1 occupies the axial position of a square-pyramidal structure, as in **D** (route **I**). This requires O^1 to be a *pivot* atom,[37] i.e., it has to be placed first in the equatorial plane of a trigonal bipyramid such as in **C** (route **I**) or **C′** (route **II**). However, while in **C** both C−Pt−O angles are expected to be around 90° (they are approximately 80° in the crystal structures of **2*cis*, 5*cis***, and **7*cis*****),** in **C′** the C^2−Pt−O^2 angle is expected to be around 120°. Therefore, this route does not allow κ^2-Aryl ⇆ κ^1-Aryl exchange in the cis isomers because **C′** would be unstable, giving **B′** after the cleavage of the Pt−O^2 bond. For the trans complexes, the intermediate **C** would give **D** and finally **E**. However, for the cis isomers there is a dissociative route **III** involving the equilibria **A′** ⇆ **B′** ⇆ **C″** ⇆ **D″** ⇆ **E″** ⇆ **F″** that would allow the fluxionality, the only condition being that the ligand L dissociates easily from the square-pyramidal intermediate **D″**. Our results establish that this condition is not met by L = XyNC (**4*cis***) or CO (**5*cis***). However, the previously reported complexes *cis*-[Pt(κ^2-Aryl)(κ^1-Aryl)(OH$_2$)] and *cis*-Me$_4$N[Pt(κ^2-Aryl)(κ^1-Aryl)(O$_2$CCF$_3$)][22] are fluxional because of the weak coordination of the ligands H_2O and $CF_3CO_2^-$.

The ^{31}P{^{1}H} NMR spectrum of **8*cis*** in $CDCl_3$ shows three singlet resonances at 6.50 ppm ($^1J_{PtP}$ = 2369 Hz), assigned to **8*cis***, 16.53 ppm ($^1J_{PtP}$ = 2579 Hz), due to **7*cis***, and −4.61 ppm assigned to PPh_3, in accordance with the equilibrium **8*cis*** ⇆ **7*cis*** + PPh_3. Correspondingly, its ^{1}H NMR spectrum in $CDCl_3$ shows five 2:1:1:1:1 MeO singlets due to **8*cis*** and two 2:1 singlets corresponding to **7*cis***. However, complex **8*trans*** is stable in solution, showing the expected ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra.

The following order of trans influence can be deduced using the $^1J_{PtC(Aryl)}$ values:[38] Aryl (640−680 Hz) > XyNC (880 Hz) > CO (977 Hz) > ON(O) (1115−1145 Hz), although slight differences with respect to this order were found using structural data (see below). The same is observed for the $^1J_{PtCO}$ value in complexes **5**: it is lower for the cis isomer (CO trans to Aryl; 1251 Hz) than for the trans (CO trans to ON(O); 2120 Hz).

The order of π-acceptor character, κ^2-Aryl ≈ PPh_3 > ON(O) ≈ κ^1-Aryl, can be deduced from the wavenumbers of the ν(CO) mode in **5*cis*** (2128 cm^{-1}), **6*trans*** (2122 cm^{-1}), **5*trans*** (2106 cm^{-1}), and **6*cis*** (2100 cm^{-1}). As in other nitroaryl derivatives,[39] all complexes show $\nu_{asym}(NO_2)$ (vs) and $\nu_{sym}(NO_2)$ (m) at 1368−1346 and 1310−1278 cm^{-1}, respectively. However, the band due to $\nu_{sym}(NO_2)$ of the coordinated nitro group in κ^2-Aryl groups, expected around 1250−1270 cm^{-1},[29] could not be assigned because in this region other bands appear when there is not a κ^2-Aryl group.

Crystal Structures. The crystal structures of complexes **2*cis*** (Figure 1), **3*cis***·$CHCl_3$ (Figure 2), **3*trans*** (Figure 3), **4*trans***·$CHCl_3$ (Figure 4), **5*cis***·CH_2Cl_2 and **5*cis***·0.5hexane (Figure 5), **6*cis*** (Figure 6), **6*trans***·$CHCl_3$ (Figure 7), **7*cis***·Me_2CO (Figure 8), and **8*trans***·$CHCl_3$ (Figure 9) have been solved. All of them show an approximately square planar geometry, although a tendency for ligands to lie alternately slightly above and below the plane (by as much as ±0.16 Å for **8*trans***) is noted for **3*cis***, **6*cis***, **6*trans***, **7*cis***, and **8*trans***. In complexes containing only κ^1-Aryl ligands, the angles at platinum are close to the ideal square-planar values and the aryl rings are tilted from the coordination plane by 69−87°. The bite angle of the chelate κ^2-Aryl ligands is significantly smaller than 90° (79.18(7)−79.94(9)°) and, correspondingly, the C(κ^2-Aryl)−Pt−C(κ^1-Aryl) angles are larger than 90° (98.83(8)−101.61(10)°). The aryl and chelate rings of the κ^2-Aryl ligands are almost parallel (interplanar angles 4−11°) and the κ^1-Aryl rings essentially perpendicular (82−90°) to the coordination plane. The last structural

(37) Purcell, K. F.; Kotz, J. C. *Inorganic Chemistry*; W. B. Saunders: London, 1977; p 404.

(38) Pregosin, P. S. *Coord. Chem. Rev.* **1982**, *44*, 247.

(39) Vicente, J.; Arcas, A.; Chicote, M. T. *J. Organomet. Chem.* **1983**, *252*, 257.

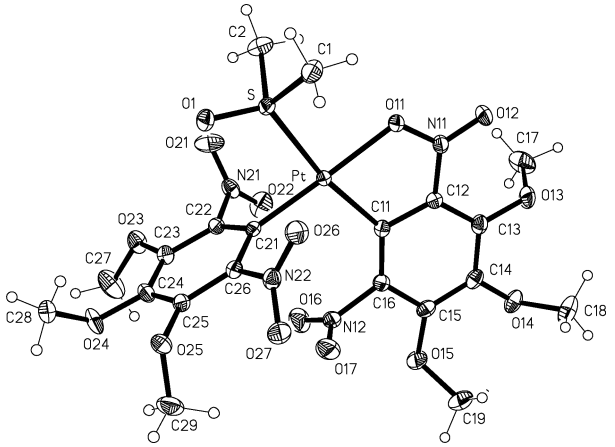


Figure 1. Ellipsoid representation of **2*cis*** (50% probability). Selected bond lengths (Å) and angles (deg): Pt−C(21) = 1.999(2), Pt−C(11) = 2.032(3), Pt−O(11) = 2.0770(18), Pt−S = 2.2930(6), S−O(1) = 1.474(2), C(12)−N(11) = 1.433(3), C(16)−N(12) = 1.478(3), N(11)−O(12) = 1.209(3), N(11)−O(11) = 1.291(3), N(12)−O(16) = 1.220(3), N(12)−O(17) = 1.224(3), C(22)−N(21) = 1.474(3), C(26)−N(22) = 1.465(3); C(21)−Pt−C(11) = 101.61(10), C(11)−Pt−O(11) = 79.74(9), C(21)−Pt−S = 87.96(7), O(11)−Pt−S = 90.70(5).

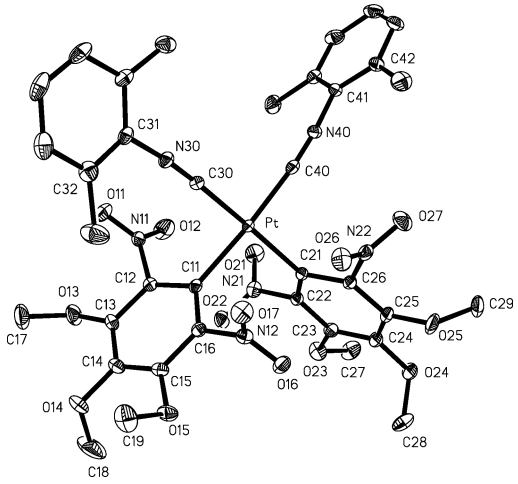


Figure 2. Ellipsoid representation of **3*cis*·**$CHCl_3$ (30% probability). The molecule of $CHCl_3$ is omitted for clarity. Selected bond lengths (Å) and angles (deg): Pt−C(30) = 1.961(2), Pt−C(40) = 1.969(2), Pt−C(21) = 2.062(2), Pt−C(11) = 2.071(2), C(12)−N(11) = 1.478(3), C(16)−N(12) = 1.477(3), C(22)−N(21) = 1.477(3), C(26)−N(22) = 1.473(3), C(30)−N(30) = 1.159(3), C(31)−N(30) = 1.398(3), C(40)−N(40) = 1.158(3), C(41)−N(40) = 1.403(3), N(11)−O(12) = 1.209(3), N(11)−O(11) = 1.228(3), N(12)−O(16) = 1.217(3), N(12)−O(17) = 1.230(3), N(21)−O(21) = 1.225(3), N(21)−O(22) = 1.226(3), N(22)−O(26) = 1.213(3), N(22)−O(27) = 1.234(3), N(21)−O(22) = 1.216(3), N(21)−O(21) = 1.224(3), N(22)−O(27) = 1.229(3), N(22)−O(26) = 1.233(3); C(30)−Pt−C(40) = 93.27(9), C(40)−Pt−C(21) = 89.76(8), C(30)−Pt−C(11) = 86.01(8), C(21)−Pt−C(11) = 91.82(8).

features agree with the aforementioned π-acceptor character of κ^2-Aryl being greater than that of κ^1-Aryl on the basis of IR data.

The Pt−C(κ^1-Aryl) bond lengths do not vary greatly, whether trans to each other (**3*trans***, 2.079(2), 2.081(2) Å; **6*trans*·**$CHCl_3$, 2.087(4), 2.088(4) Å; **8*trans*·**0.5$CHCl_3$, 2.089(2), 2.094(2) Å), to CO (**3*trans***, 2.079(2), 2.081(2) Å; **6*cis***, 2.0867(19) Å), or to PPh_3 (**6*cis***, 2.0964(17) Å). However, they are slightly or significantly shorter when they are trans to an isonitrile (**3*cis*·**$CHCl_3$, 2.062(2), 2.071(2) Å) or to the O-nitro group in **2*cis***, **5*cis***, and **7*cis*** (1.997(2)−2.009(3) Å), respectively, due to the order of trans influence κ^1-Aryl ≈ CO ≈ PPh_3 > XyNC ≫ ON(O). Similarly, the Pt−C(κ^2-Aryl) bond distances are not significantly different, despite being trans to *S*-dmso (**2*cis***, 2.032(3) Å), CO (**5*cis*·**CH_2Cl_2, 2.033(3) Å; **5*cis*·**0.5(hexane), 2.0397(18) Å), or PPh_3 (**7*cis***, 2.045(2) Å). In view of the larger esd's of **4*trans*** (see Experimental Section), it would be

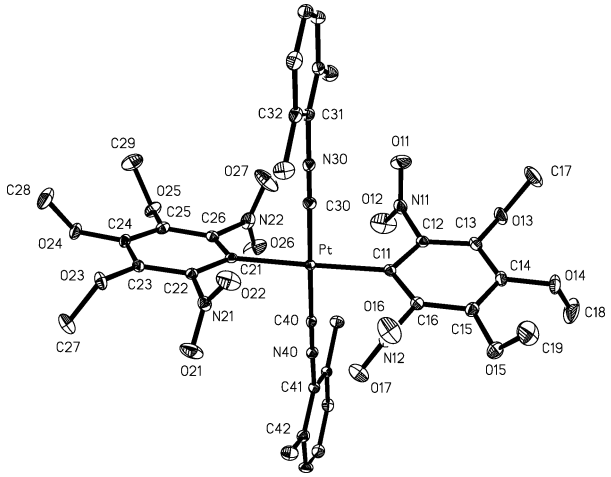


Figure 3. Ellipsoid representation of **3*trans*** (30% probability). Selected bond lengths (Å) and angles (deg): Pt−C(40) = 1.951(2), Pt−C(30) = 1.954(3), Pt−C(11) = 2.079(2), Pt−C(21) = 2.081(2), C(12)−N(11) = 1.475(3), C(16)−N(12) = 1.480(3), C(22)−N(21) = 1.473(3), C(26)−N(22) = 1.479(3), C(30)−N(30) = 1.143(3), C(31)−N(30) = 1.410(3), C(40)−N(40) = 1.149(3), C(41)−N(40) = 1.403(3), N(11)−O(12) = 1.200(3), N(11)−O(11) = 1.218(3), N(12)−O(16) = 1.206(3), N(12)−O(17) = 1.221(3), N(21)−O(22) = 1.210(3), N(21)−O(21) = 1.218(3), N(22)−O(26) = 1.208(3), N(22)−O(27) = 1.222(3); C(40)−Pt−C(11) = 89.38(9), C(30)−Pt−C(11) = 90.27(9), C(40)−Pt−C(21) = 91.02(9), C(30)−Pt−C(21) = 89.29(9).

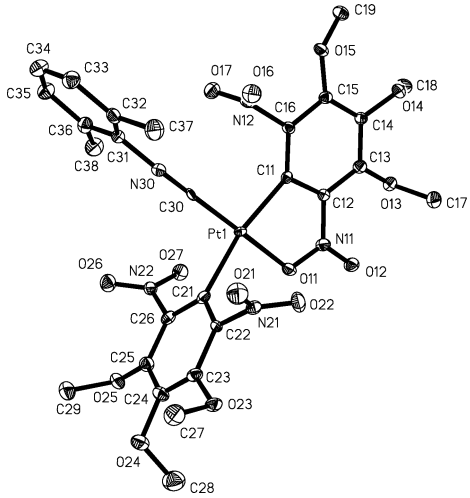


Figure 4. Ellipsoid representation of one of four independent molecules of **4*trans*·**$CHCl_3$ (30% probability). The molecule of $CHCl_3$ is omitted for clarity. Selected bond lengths (Å) and angles (deg) (average of four values): Pt(1)−C(11) = 2.035, Pt(1)−C(21) = 2.084, Pt(1)−C(30) = 1.868, Pt(1)−O(11) = 2.047, C(12)−N(11) = 1.429, C(16)−N(12) = 1.494, C(22)−N(21) = 1.466, C(26)−N(22) = 1.486, C(30)−N(30) = 1.160, C(31)−N(30) = 1.413, N(11)−O(11) = 1.286, N(11)−O(12) = 1.220, N(12)−O(16) = 1.213, N(12)−O(17) = 1.219, N(21)−O(21) = 1.238, N(21)−O(22) = 1.205, N(22)−O(26) = 1.182, N(22)−O(27) = 1.235; C(30)−Pt(1)−C(11) = 101.4, O(11)−Pt(1)−C(11) = 86.9, C(30)−Pt(1)−C(21) = 89.9, O(11)−Pt(1)−C(21) = 86.9, C(30)−N(30)−C(31) = 169.2, N(30)−C(30)−Pt(1) = 175.3.

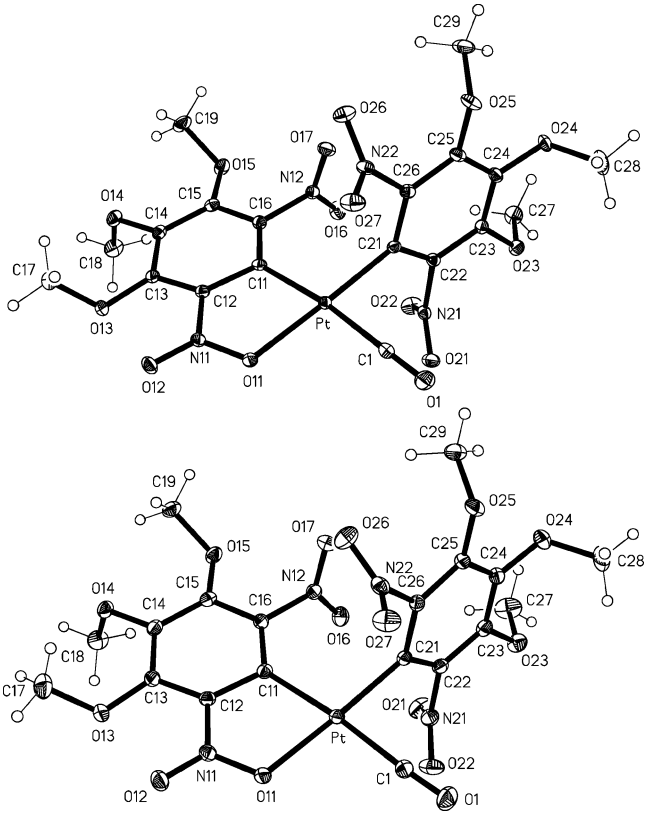


Figure 5. Ellipsoid representations of **5*cis***: (top) dichloromethane solvate, 30% probability; (bottom) hexane hemisolvate, 50% probability. The two forms are not isostructural. The solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg) for **5*cis***·CH_2Cl_2: Pt−C(1) = 1.937(3), Pt−C(21) = 2.009(3), Pt−C(11) = 2.033(3), Pt−O(11) = 2.079(2), C(1)−O(1) = 1.118(4), C(12)−N(11) = 1.431(4), C(16)−N(12) = 1.476(4), C(22)−N(21) = 1.481(4), C(26)−N(22) = 1.469(4), O(11)−N(11) = 1.295(3), O(12)−N(11) = 1.206(3), O(16)−N(12) = 1.220(4), O(17)−N(12) = 1.225(3), O(21)−N(21) = 1.221(4), O(22)−N(21) = 1.218(4), O(26)−N(22) = 1.225(4), O(27)−N(22) = 1.228(4); C(1)−Pt−C(21) = 85.66(13), C(21)−Pt−C(11) = 100.32(12), C(1)−Pt−O(11) = 94.43(11), C(11)−Pt−O(11) = 79.74(10), O(1)−C(1)−Pt = 178.0(3). The bond lengths and angles for **5*cis***·0.5hexane are not significantly different from those for **5*cis***·CH_2Cl_2; a least-squares fit of both molecules (omitting hydrogens, terminal O of uncoordinated nitro groups, and terminal C of methoxy groups) gave an rms deviation of 0.12 Å.

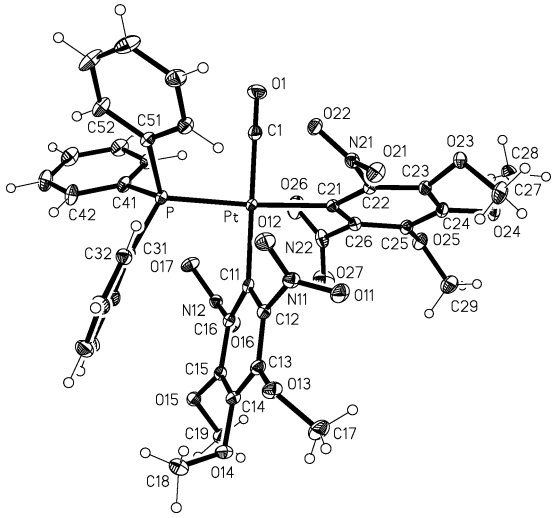


Figure 6. Ellipsoid representation of **6*cis*** (30% probability). Selected bond lengths (Å) and angles (deg): Pt−C(1) = 1.909(2), Pt−C(11) = 2.0867(19), Pt−C(21) = 2.0964(17), Pt−P = 2.3303(4), O(1)−C(1) = 1.123(2), O(11)−N(11) = 1.231(2), O(12)−N(11) = 1.226(2), O(16)−N(12) = 1.225(2), O(17)−N(12) = 1.2227(19), O(21)−N(21) = 1.222(2), O(22)−N(21) = 1.2304(19), O(26)−N(22) = 1.219(3), O(27)−N(22) = 1.214(3), N(11)−C(12) = 1.472(2), N(12)−C(16) = 1.477(2), N(21)−C(22) = 1.470(2), N(22)−C(26) = 1.470(2); C(1)−Pt−C(21) = 86.90(7), C(11)−Pt−C(21) = 92.47(7), C(1)−Pt−P = 90.58(6), C(11)−Pt−P = 90.47(5), O(1)−C(1)−Pt = 176.14(18).

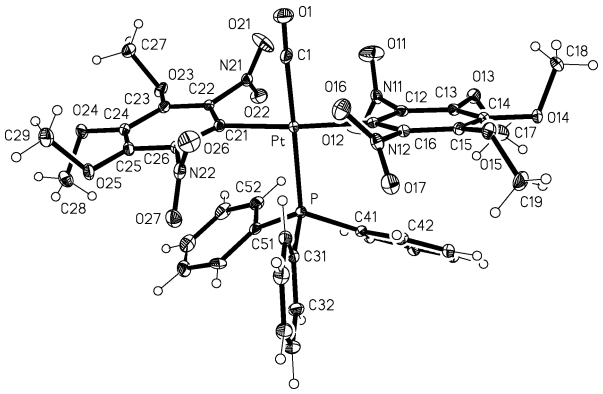


Figure 7. Ellipsoid representation of **6*trans***·$CHCl_3$ (30% probability). Selected bond lengths (Å) and angles (deg): Pt−C(1) = 1.935(5), Pt−C(21) = 2.087(4), Pt−C(11) = 2.088(4), Pt−P = 2.3312(12), O(1)−C(1) = 1.087(6), O(11)−N(11) = 1.199(6), O(12)−N(11) = 1.185(6), O(16)−N(12) = 1.223(6), O(17)−N(12) = 1.224(6), O(21)−N(21) = 1.214(6), O(22)−N(21) = 1.203(6), O(26)−N(22) = 1.213(6), O(27)−N(22) = 1.216(6), N(11)−C(12) = 1.478(6), N(12)−C(16) = 1.467(6), N(21)−C(22) = 1.482(6), N(22)−C(26) = 1.472(6); C(1)−Pt−C(21) = 89.40(19), C(1)−Pt−C(11) = 89.55(19), C(21)−Pt−P = 91.39(13), C(11)−Pt−P = 90.55(12), O(1)−C(1)−Pt = 174.9(5).

inadvisable to overinterpret small differences, but it seems clear that the Pt−C(κ^2-Aryl) (average 2.035 Å) and Pt−C(κ^1-Aryl) (average 2.084 Å) distances are in the ranges found for the other complexes containing these ligands trans to aryl, CO, PPh_3, or *S*-dmso (2.032(3)−2.045(2) and 2.079(2)−2.0964(17) Å, respectively). For all these complexes, the Pt−C(κ^2-Aryl) bond lengths are shorter than the Pt−C(κ^1-Aryl) bond lengths due to the aforementioned greater π-acceptor character of the κ^2-Aryl ligand. However, the Pt−(κ^1-Aryl) lengths in **2*cis***, **5*cis***·CH_2Cl_2, **5*cis***·0.5(hexane), and **7*cis*** (1.999(2), 2.009(3), 2.0069(18), and 1.997(2) Å, respectively) are shorter than the corresponding Pt−C(κ^2-Aryl) distances (2.032(3), 2.033(3), 2.0397(18), and 2.045(2) Å, respectively), as a consequence of the weaker trans influence of the O-nitro ligand compared to that of CO, XyNC, PPh_3, or *S*-dmso ligands. The greater π-acceptor character of the κ^2-Aryl as compared to that of κ^1-Aryl is also shown by the Pt−CO bond length in **5*cis*** (1.937(3), 1.939(2) Å) being significantly longer than in **6*cis*** (1.909(2) Å). However, although this should produce in **6*cis*** an increase in the C−O bond distance with respect to **5*cis***, the increase is not significant: 1.123(2) vs 1.118(4) Å. Similarly, the greater π-acceptor character of PPh_3 as compared to that of κ^1-Aryl can explain the observation that the Pt−CO and PtC−O bond lengths in the complex **6*cis*** (1.909(2) and 1.123(2) Å) are significantly shorter and longer, respectively, than the corresponding distances in **6*trans*** (1.935(5) and 1.087(6) Å). Both Pt−CO bond lengths should be similar if only the trans influences of κ^1-Aryl and PPh_3 are considered.

The Pt−C_{CNXy} (trans to κ^1-Aryl, **3*cis*** 1.961(2), 1.969(2) Å; trans to XyNC, **3*trans*** 1.951(2), 1.954(3) Å; trans to ON(O), **4*trans*** average of four molecules 1.868 Å), the Pt−O (trans to

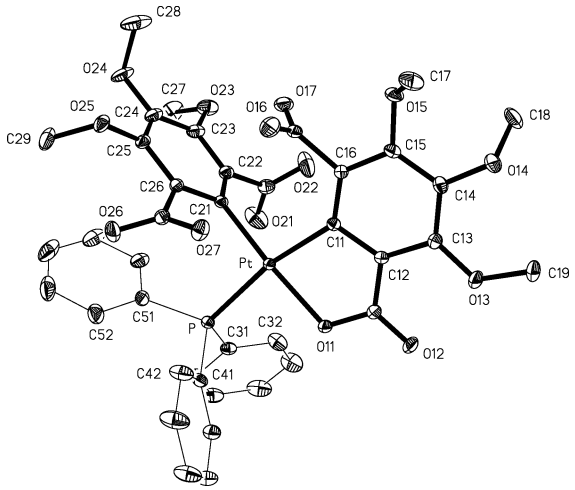


Figure 8. Ellipsoid representation of **7*cis***·Me_2CO (50% probability; solvent omitted). Selected bond lengths (Å) and angles (deg): Pt−C(21) = 1.997(2), Pt−C(11) = 2.045(2), Pt−O(11) = 2.0789(14), Pt−P = 2.3074(6), O(11)−N(11) = 1.300(2), O(12)−N(11) = 1.219(2), O(16)−N(12) = 1.225(3), O(17)−N(12) = 1.213(3), O(21)−N(21) = 1.209(3), O(22)−N(21) = 1.206(3), O(26)−N(22) = 1.226(2), O(27)−N(22) = 1.223(2), C(12)−N(11) = 1.424(3), C(16)−N(12) = 1.482(3), C(22)−N(21) = 1.482(3), C(26)−N(22) = 1.463(3); C(21)−Pt−C(11) = 98.83(8), C(11)−Pt−O(11) = 79.18(7), C(21)−Pt−P = 92.20(6), O(11)−Pt−P = 90.12(4).

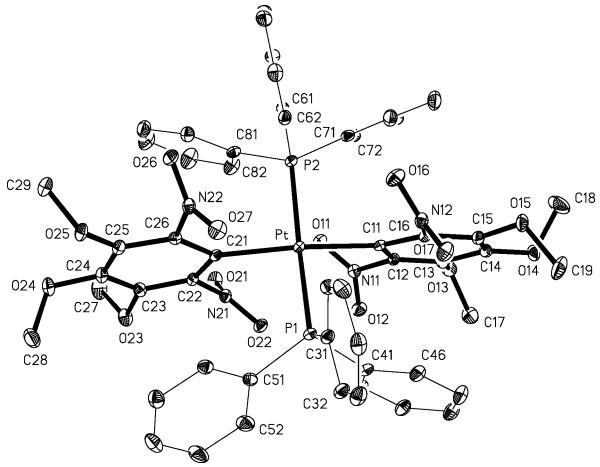


Figure 9. Ellipsoid representation of **8*trans***·0.5$CHCl_3$ (50% probability; solvent omitted). Selected bond lengths (Å) and angles (deg): Pt−C(11) = 2.089(2), Pt−C(21) = 2.094(2), Pt−P(2) = 2.3267(7), Pt−P(1) = 2.3397(7), C(12)−N(11) = 1.475(3), C(16)−N(12) = 1.475(3), C(22)−N(21) = 1.474(3), C(26)−N(22) = 1.481(3), O(11)−N(11) = 1.228(3), O(12)−N(11) = 1.228(3), O(16)−N(12) = 1.225(3), O(17)−N(12) = 1.227(3), O(21)−N(21) = 1.221(3), O(22)−N(21) = 1.230(3), O(26)−N(22) = 1.230(3), O(27)−N(22) = 1.224(3); C(11)−Pt−P(2) = 89.92(7), C(21)−Pt−P(2) = 90.81(7), C(11)−Pt−P(1) = 89.42(7), C(21)−Pt−P(1) = 90.83(7).

κ^1-Aryl, **2*cis*** 2.0770(18) Å, **5*cis*** 2.079(2) Å, **7*cis*** 2.0789(14) Å; trans to XyNC, **4*trans*** average of four molecules 2.047 Å), and the Pt−P bond distances (trans to κ^1-Aryl, **6*cis*** 2.3303(4) Å; trans to CO, **6*trans*** 2.3312(12) Å; trans to PPh_3, **8*trans*** 2.3267(7), 2.3397(7) Å) reveal the same aforementioned order of trans influence: κ^1-Aryl ≈ CO ≈ PPh_3 > XyNC ≫ ON(O). The π-acceptor character of the κ^2-Aryl ligand should cause a lengthening of the trans Pt−P bond in **7*cis*** with respect to **6*cis***. However, since the bond is shorter in **7*cis*** (2.3074(6) Å), we can only explain it by assuming that trans influence κ^1-Aryl > κ^2-Aryl.

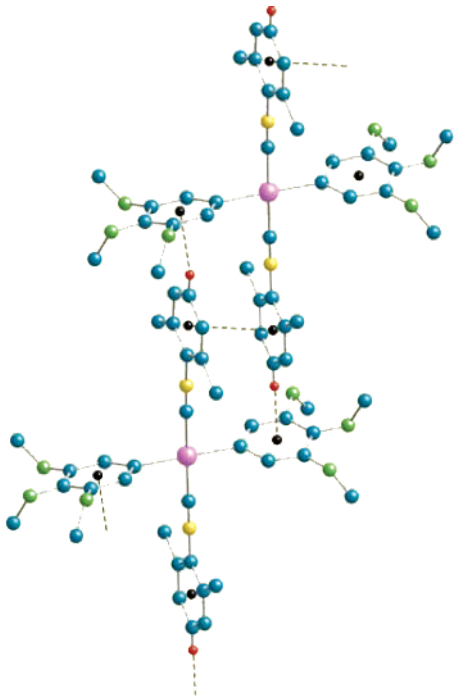


Figure 10. Association of molecules of **3*trans*** via $\pi\cdots\pi$ stacking of XyNC rings and C−H$\cdots\pi$ interactions to give a chain. All NO_2 groups, hydrogen atoms (except those involved in the C−H$\cdots\pi$ interactions), and κ^2-Aryl atoms (except the C and O atoms bonded to Pt) have been omitted for clarity.

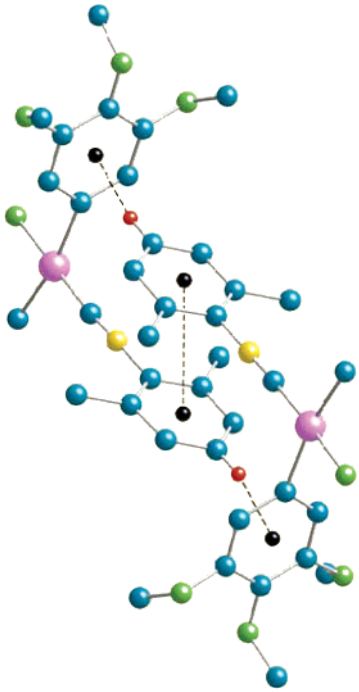


Figure 11. Association of two molecules of **4*trans***·$CHCl_3$ via $\pi\cdots\pi$ stacking of XyNC rings and C−H$\cdots\pi$ interactions. All NO_2 groups, hydrogen atoms (except those involved in the C−H$\cdots\pi$ interactions), and κ^2-Aryl atoms (except the C and O atoms bonded to Pt) have been omitted for clarity.

In the complex **2*cis***, the geometry of the dimethyl sulfoxide moiety is virtually unaffected by S coordination and the S−O bond length (1.474(2) Å) is similar to that in solid dimethyl sulfoxide, determined at −60 °C (1.471(8) Å).[40] The Pt−S bond

(40) Viswamitra, M. A.; Kannan, K. K. *Nature* **1966**, *209*, 1016.

distance (2.2930(6) Å) lies in the range reported in other aryl Pt(II) complexes containing an *S*-dmso ligand bonded trans to an aryl group (2.2693(5)−2.324(2) Å),[18,41,42] but is longer than those in aryl Pt(II) complexes with an *S*-dmso ligand bonded trans to N[42,43] or O,[44] as a consequence of the trans influence of an aryl group being stronger than that of a N or O donor ligand.

As has been observed previously in other nitroaryl complexes,[22,24,29,45] the N−O(Pt) bond distance is longer (average 1.293 Å) than the others (average 1.216 Å).

All of the complexes display a variety of contacts in their packing (e.g. C−H···O interactions, solvent Cl···O, axial Pt···O), but a full description would be extremely long. Instead, we present one motif associated with the XyNC ligand; the molecules associate in dimers with a $\pi\cdots\pi$ stacking of the XyNC rings[46] and a short contact from the para hydrogen of the XyNC ring to the centroid of κ^1-Aryl. In **3*cis*** the rings are parallel by symmetry, have an intercentroid distance of 3.62 Å, a perpendicular distance of 3.44 Å, and an offset of 1.1 Å, and the H···Cent distance (C21−C26) is 2.66 Å. For **3*trans*** (see Figure 10) both XyNC rings are involved in such interactions, leading to a chain of molecules parallel to the *y* axis. For rings C31−C36 and C41−C46, the corresponding values are 3° and 3.58, 3.42, and 1.1 Å and H···Cent = 2.48 (C11−C16), 2.50 Å (C21−C26). Molecules 1 and 2 of the four present in the asymmetric unit cell of **4*trans***·$CHCl_3$ form a "dimer" through such $\pi\cdots\pi$ stacking/CH···π contacts (Figure 11). The centroid−centroid distance is 3.82 Å, the perpendicular distance 3.50 Å, the interplanar angle 2°, and the centroid offset 1.5 Å. The H···Cent distance is 2.68 Å for both molecules.

Color of the Complexes. In agreement with previous observations,[22,24] complexes with a κ^2-Aryl ligand have intense colors (yellow (**5*cis***), red (**5*trans***), and orange (**2*cis***, **4*cis***, **4*trans***, and **7*cis***)), while in those having only κ^1-Aryl ligands, these colors fade to pale yellow (**3*cis***, **3*trans***, **6*cis***, **6*trans***, **8*cis***, and **8*trans***).

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Supporting Information Available: CIF files for **2*cis***, **3*cis***·$CHCl_3$, **3*trans***, **4*trans***·$CHCl_3$, **5*cis***·CH_2Cl_2, **5*cis***·0.5(hexane), **6*cis***, **6*trans***·$CHCl_3$, **7*cis***·Me_2CO, and **8*trans***·0.5$CHCl_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(41) Minghetti, G.; Doppiu, A.; Stoccoro, S.; Zucca, A.; Cinellu, M. A.; Manassero, M.; Sansoni, M. *Eur. J. Inorg. Chem.* **2002**, 431. Owen, J. S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2004**, *126*, 8247.

(42) Zucca, A.; Doppiu, A.; Cinellu, M. A.; Stoccoro, S.; Minghetti, G.; Manassero, M. *Organometallics* **2002**, *21*, 783.

(43) Cave, G. W. V.; Alcock, N. W.; Rourke, J. P. *Organometallics* **1999**, *18*, 1801. Ryabov, A. D.; Otto, S.; Samuleev, P. V.; Polyakov, V. A.; Alexandrova, L.; Kazankov, G. M.; Shova, S.; Revenco, M.; Lipkowski, J.; Johansson, M. H. *Inorg. Chem.* **2002**, *41*, 4286.

(44) Izakovich, E. N.; Kachapina, L. M.; Shibaeva, R. P.; Khidekel, M. L. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1983**, 1389.

(45) Vicente, J.; Arcas, A.; Borrachero, M. V.; de Goicoechea, M. L.; Lanfranchi, M.; Tiripicchio, A. *Inorg. Chim. Acta* **1990**, *177*, 247. Vicente, J.; Arcas, A.; Borrachero, M. V.; Tiripicchio, A.; Tiripicchio-Camellini, M. *Organometallics* **1991**, *10*, 3873.

(46) Gupta, B. D.; Yamuna, R.; Mandal, D. *Organometallics* **2006**, *25*, 706. Janiak, C. *Dalton Trans.* **2000**, 3885. Okawa, H. *Coord. Chem. Rev.* **1998**, *92*, 1.