Compound [$PtPh_2(SMe_2)_2$] as a Versatile Metalating Agent in the Preparation of New Types of [C,N,N′] Cyclometalated Platinum Compounds

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The reactions of [$PtPh_2(SMe_2)_2$] (**1**) with ligands $RCH{=}NCH_2CH_2NMe_2$ (R = C_6H_5 (**2a**), 2-BrC_6H_4 (**2b**), 2,6-$Cl_2C_6H_3$ (**2c**), 2-ClC_6H_4 (**2d**), and C_6F_5 (**2e**)) produced compounds [$PtPh_2\{Me_2NCH_2CH_2NCHR\}$] (**3**). Compounds **3** led to formation of three different types of [C,N,N′] platinum compounds, including platinum(II) compounds with a seven-membered metallacycle. The reactions of the cyclometalated compounds with triphenylphosphine were also studied.

Cyclometalated compounds containing nitrogen ligands have been widely studied due to their potential applications in several areas such as organic synthesis, homogeneous catalysis, and the design of new materials with interesting properties.[1] In recent years, in addition to classical bidentate [C,N] systems, interest has been focused on cyclometalated platinum compounds containing [C,N,N′][2−8] or [N,C,N][9−12] terdentate monoanionic ligands.

Diarylplatinum(II) complexes containing readily displaced dialkylsulfide ligands have been extensively used as precursors of several types of platinum compounds.[13−17] The present paper deals with the reactions of potentially terdentate [C,N,N′] ligands $RCH{=}NCH_2CH_2NMe_2$ (R = C_6H_5, 2-BrC_6H_4, 2,6-$Cl_2C_6H_3$, 2-ClC_6H_4, and C_6F_5) with platinum substrate [$PtPh_2(SMe_2)_2$] in order to compare the results with those obtained for [C,N] ligands,[16] as well as with those reported when [$Pt_2Me_4(\mu\text{-}SMe_2)_2$][3] was used as starting material.

The reaction of [$PtPh_2(SMe_2)_2$] with $C_6H_5CH{=}NCH_2CH_2NMe_2$ (**2a**) in toluene at room temperature produced compound [$PtPh_2(Me_2NCH_2CH_2NCHC_6H_5)$] (**3a**) containing a bidentate [N,N′] ligand. Cyclometalation of the coordinated ligand **2a** was not observed at room temperature; however, when a toluene solution of compound **3a** was refluxed for several hours, the cyclometalated platinum(II) compound [$PtPh(Me_2NCH_2CH_2NCHC_6H_4)$] (**4a**) containing a terdentate [C,N,N′] ligand was obtained in fair yield.

The reaction of [$PtPh_2(SMe_2)_2$] (**1**) with 2-$BrC_6H_4CH{=}NCH_2CH_2NMe_2$ (**2b**) in toluene at room temperature produced the cyclometalated [C,N,N′] platinum(IV) complex [$PtBrPh_2(Me_2NCH_2CH_2NCHC_6H_4)$] (**5b**), which indicates that oxidative addition of C−Br is fast, in agreement with the higher reactivity of C−Br versus C−H bonds.[18] Intermediate coordination compound [$PtPh_2\{Me_2NCH_2CH_2NCH(2\text{-}BrC_6H_4)\}$] (**3b**) could be detected by ^1H NMR spectroscopy in $CDCl_3$.[19] Despite the susceptibility of triarylplatinum(IV) species to un-

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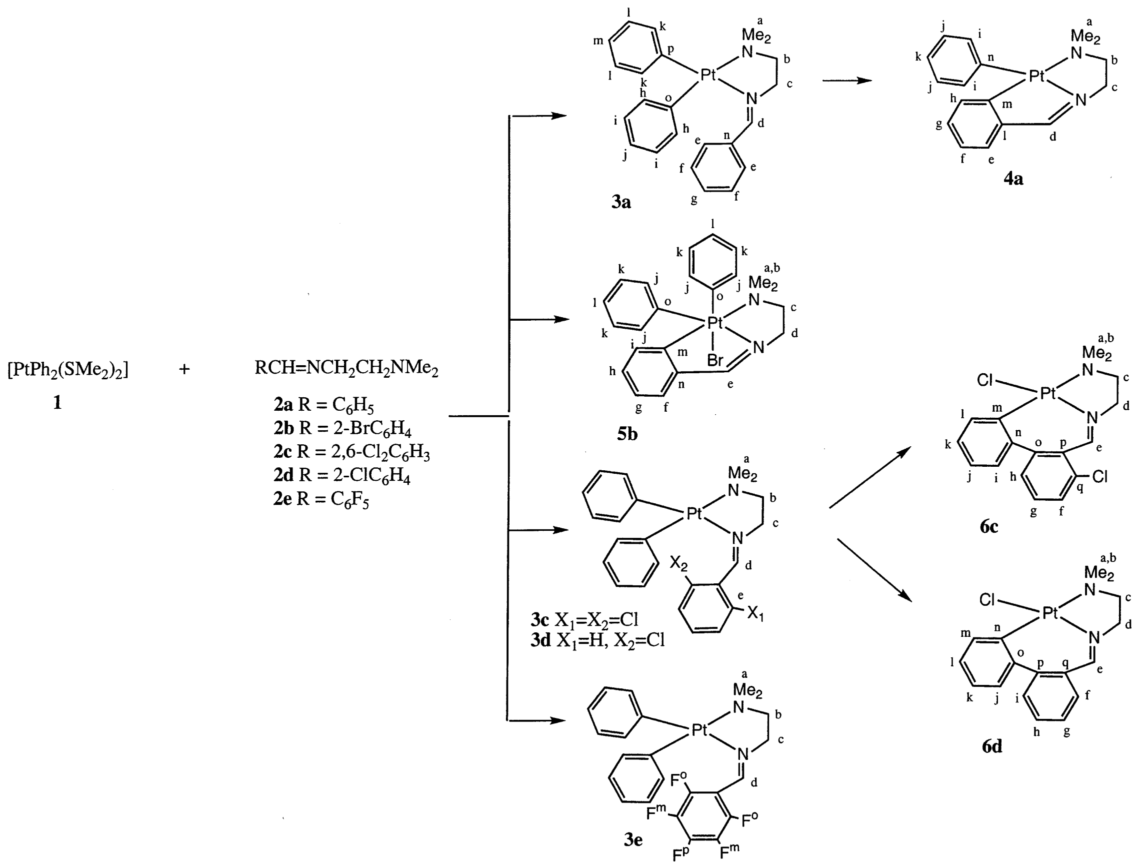
Scheme 1



dergo reductive elimination of biaryl,[12,20] no evidence of reductive elimination of biphenyl from **5b** to yield a platinum(II) compound was observed.

The reactions of [$PtPh_2(SMe_2)_2$] with ligands 2,6-$Cl_2C_6H_3CH{=}NCH_2CH_2NMe_2$ (**2c**), 2-$ClC_6H_4CH{=}NCH_2CH_2NMe_2$ (**2d**), and $C_6F_5CH{=}NCH_2CH_2NMe_2$ (**2e**) in toluene gave coordination compounds **3c**, **3d**, and **3e**, in which the ligand behaves as bidentate [N,N′] ligands. A 2D-NOESY NMR was carried out for **3e**, and the presence of a cross-peak signal between the imine (H^d) and the methylene (H^c) protons supports a *trans* arrangement (*E* configuration)[21] across the C=N bond, as observed in the structure determination carried out for **3a** (see below).

Intramolecular activation of C−Cl or C−F bonds was not observed at room temperature, in agreement with their lower reactivity when compared to C−Br bonds. Therefore, toluene solutions of compounds **3c**−**e** were refluxed for several hours. For **3e**, formation of the corresponding platinum(IV) cyclometalated compound was not observed. The lack of reactivity of the C−F bond, which has been however activated upon reaction of ligand **2e** with platinum substrate [$Pt_2Me_4(\mu\text{-}SMe_2)_2$],[22] can be related to the combined effects of the inertness of the C−F bond[23] and the unfavorable steric effects of the phenyl groups. In contrast, upon refluxing in toluene for 2 h **3c** and **3d** gave, respectively, compounds [$PtCl(Me_2NCH_2CH_2NCHC_6ClH_3C_6H_4)$] (**6c**) and [$PtCl(Me_2NCH_2CH_2NCHC_6H_4C_6H_4)$] (**6d**), depicted in Scheme 1, which represent a new class of [C,N,N′] cyclometalated platinum(II) compound containing a seven-membered metallacycle. In view of these results, the behavior of the compound [$PtBrPh_2(Me_2NCH_2CH_2NCHC_6H_4)$] (**5b**) in refluxing toluene was also studied, but no compound with a spectral pattern analogous to that of compounds **6** was detected. The failure to transform **5b** into a seven-membered metallacycle can be related to the low tendency of the chelate dinitrogen ligand to dissociate and produce the required vacant site in the coordination sphere of the platinum.

All compounds were characterized by elemental analyses, FAB mass spectra, and NMR spectroscopies, and compounds **3a** and **4a** were also characterized crystallographically. In the ^1H NMR spectra, the dimethylamino protons and the imine proton are coupled to platinum, thus confirming coordination of both nitrogen atoms to platinum. For compounds **6**, the large value of $J(H{-}Pt)$ for the imine (149 Hz) is consistent with the presence of a chloro ligand *trans* to the imine. The {$^1H-^{13}C$}-heterocorrelation spectra of **3a**, **4a**, **5b**, **6c**, and **6d** showed respectively 9, 7, 10, 7, and 8 cross-peaks in the aromatic region. These results are consistent with the

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[19] Resonances at $\delta = 2.65$ [s, $J(Pt{-}H) = 21$, NMe_2] and $\delta = 8.98$ [s, $J(Pt{-}H) = 41$, CHN] were assigned to **3b**. Other resonances could not be assigned due to overlapping with those of **2b** and **5b**.

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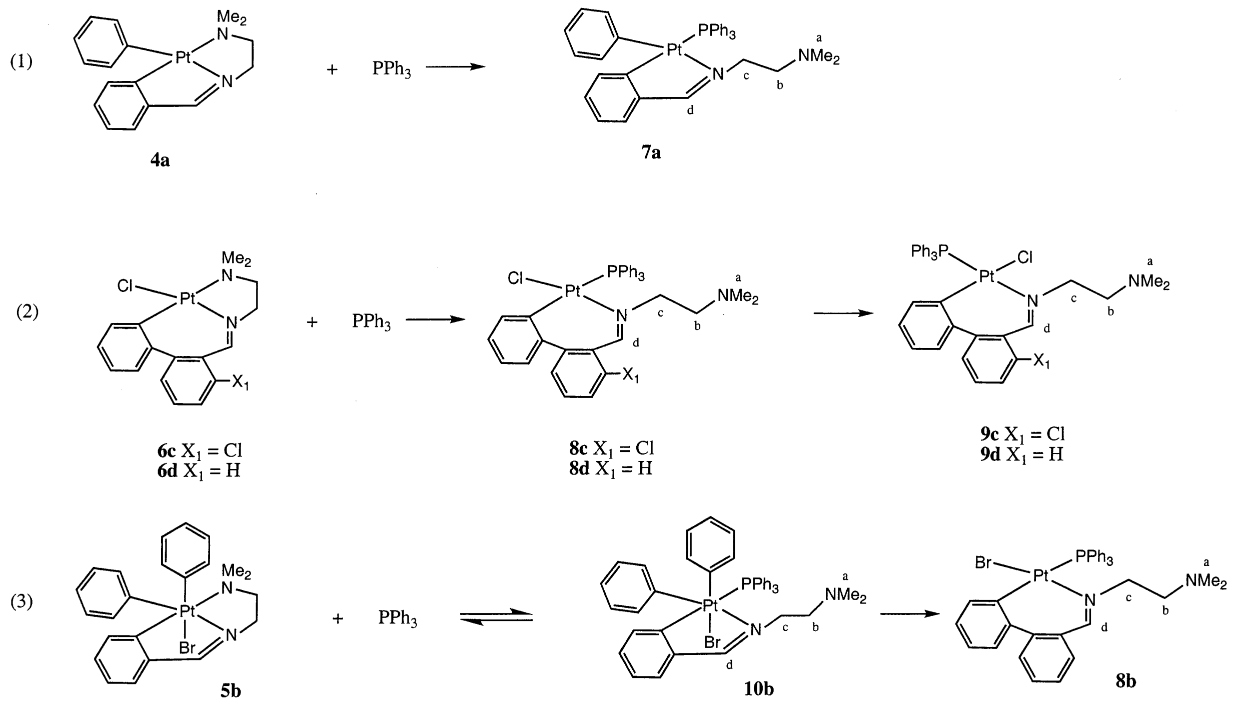
Scheme 2



proposed structures, in particular with the nonequivalence of the two η^1-phenyl ligand in **3a** and **5b**. The ^{195}Pt resonances are in the expected range for the corresponding set of ligands and oxidation state of the platinum center. Complete NMR data and the {^{1}H−^{13}C}-heterocorrelation spectrum of **6c** (Figure S1) are given in the Supporting Information.

The reactions of the new cyclometalated compounds (**4a**, **5b**, **6c**, and **6d**) with triphenylphosphine were studied in order to analyze the lability of the dimethylamino group as well as the stability of the metallacycles.[24,25]

The reaction of **4a** with an equimolecular amount of PPh_3 carried out in acetone at room temperature produced compound $[PtPh(Me_2NCH_2CH_2NCHC_6H_4)(PPh_3)]$ (**7a**), in which the triphenylphosphine replaces the dimethylamino group. As shown in Scheme 2, a similar reaction for compounds **6c** and **6d** produces respectively compounds $[PtCl(Me_2NCH_2CH_2NCHC_6ClH_3C_6H_4)(PPh_3)]$ (**8c**) and $[PtCl(Me_2NCH_2CH_2NCHC_6H_4C_6H_4)(PPh_3)]$ (**8d**), which isomerize in solution to yield within a few hours compounds **9c** and **9d**. In contrast, isomerization was not observed for **7a**. Cyclometalated [C,N] compounds **7**, **8**, and **9** do not react further with phosphine, which indicates that the corresponding metallacycles are not cleaved.

Compounds **8c** and **8d** were characterized by NMR in solution, and compounds **7a**, **9c**, and **9d** were characterized by elemental analyses, FAB mass spectra, and NMR spectroscopies. Compound **9c** was also characterized crystallographically. The value of the coupling J(P−Pt) observed in ^{31}P and ^{195}Pt NMR spectra increases significantly from compounds **8** (J(P−Pt) ca. 1800 Hz), in which the triphenylphosphine is *trans* to the metalated ring, to compounds **9** (J(P−Pt) ca. 4300 Hz), in which the triphenylphosphine is *trans* to the imine. Consistently, the imine proton appears as a singlet for compounds **8** and as a doublet due to coupling with ^{31}P for compounds **9**.

The obtained geometries for **7a** (PPh_3 *trans* to the metalated carbon) and for **9c** and **9d** (PPh_3 *trans* to the imine) are in good agreement with the *transphobia*[26] and the *trans-choice*[27] models.

The reaction of compound **5b** with triphenylphosphine under the conditions reported for compounds **4** and **6** led to nearly quantitative recovery of the initial compound **5b**, indicating a high stability of the terdentate [C,N,N′] platinum(IV) compound. When this reaction was followed by ^{1}H and ^{31}P NMR in solution, formation of the expected platinum(IV) compound **10b** in a 30% yield was observed within 1 h. [28] After 24 h, the intensity of the NMR signals corresponding to **10b** decreased, while new signals corresponding to a platinum(II) compound with one triphenylphosphine ligand appeared and were tentatively assigned to **8b** (relative amounts **8b**:**10b** = 2:1). After 48 h, according to ^{31}P NMR, unreacted **5b** was still the major component (ca. 70%), and, in addition to **8b**, very minor resonances corresponding to a compound with two mutually *trans* PPh_3 ligands (**11b**) were observed. These results support the suggestion that a vacant site in the coordination sphere of platinum is required for the process leading to seven-membered metallacycles. This process takes place for **5b** only in the presence of PPh_3, which induces the dissociation of the dimethylamino arm of the ter-

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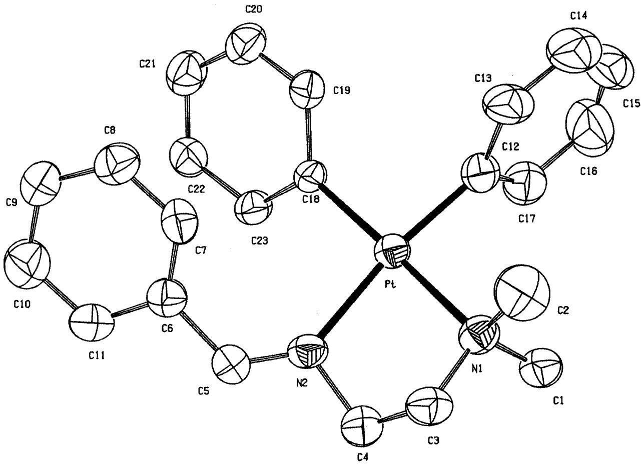


Figure 1. Molecular structure of compound **3a**.

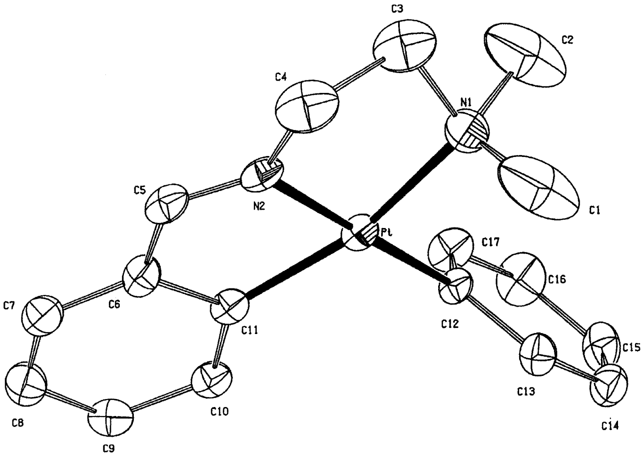


Figure 2. Molecular structure of compound **4a**.

dentate ligand and favors the formation of the corresponding compound **8**. A similar result has been described for compound [$PtBrPh_2(PhCH_2NCHC_6H_4)(SMe_2)$],[16] in which prior dissociation of the SMe_2 ligand is required for the formation of a seven-membered metallacycle.

Crystal Structures. Suitable crystals of compounds **3a** and **4a** were grown from acetone solution. Crystals of **9c** were obtained upon slow difusion of hexane into an acetone solution of the compound. The crystal structures are composed of discrete molecules separated by van der Waals distances. The structures are shown in Figures 1, 2, and 3, and selected molecular dimensions are listed in Table 1. The molecular structures confirm the geometries predicted from spectroscopic data.

For **3a**, the imine is coordinated through both nitrogen atoms to platinum and adopts an *E* configuration, the torsion angle C(4)−N(2)−C(5)−C(6) being 172.39°. The phenyl ligands are tilted from the coordination plane by 87.30° (Ph *trans* to imine) and 48.27° (Ph *trans* to amine), being rotated by 82.75° to each other.

For **4a** a fused [5,5,6] tricyclic system containing a five-membered metallacycle, a chelate ring with two nitrogen atoms, and the phenyl group results from terdentate [C,N,N′] coordination of the ligand. The metallacycle contains the imine functionality and is approximately planar; the largest deviation from the mean plane defined by the five atoms is −0.0240 Å for C(11). The dihedral angle between the mean planes of the metallacycle and the coordination plane is 22.20°, and the phenyl ligand is tilted from the coordination plane by 81.68°.

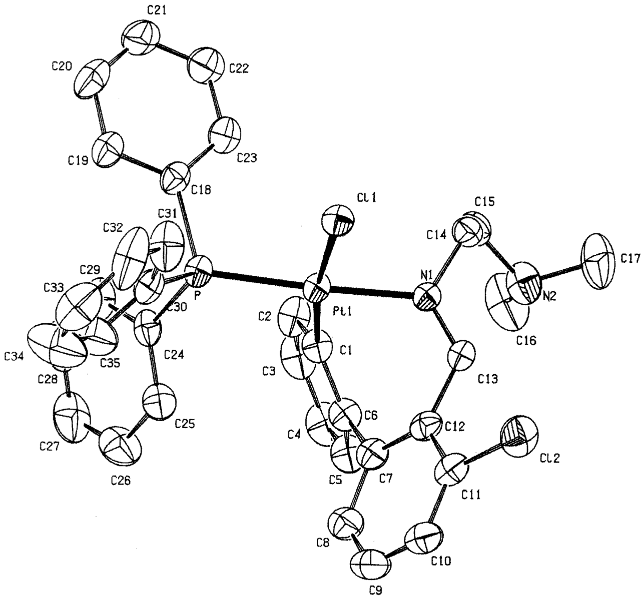


Figure 3. Molecular structure of compound **9c**.

For **9c**, a nonplanar seven-membered metallacycle in which the two phenyl rings are tilted 52.30(2)° from each other results from bidentate [C,N] coordination. The triphenylphosphine is *trans* to the imine group, and the uncoordinated NMe_2 moiety points away from the platinum center.

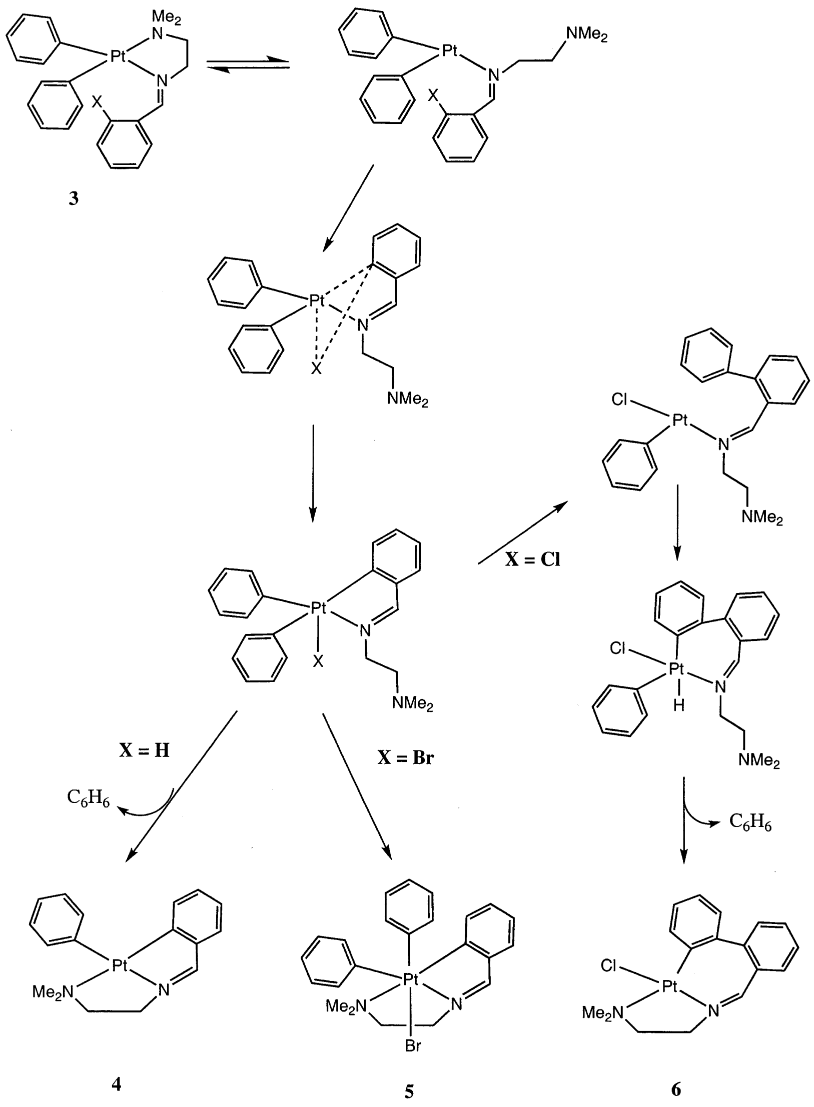
Bond lengths and angles are well within the range of values obtained for analogous compounds. In particular, the Pt−C bonds are in the range of values found for other aryl complexes of platinum(II)[13,17b] and the Pt−amine distances are larger than platinum−imine distances, consistent with the weaker ligating ability of amines for platinum.[3,7,22] Most bond angles at platinum are close to the ideal value of 90°, and the smallest angles correspond to N(2)−Pt−N(1) (81.3(3)° for **3a** and 81.0(2)° for **4a**) and to the metallacycle (C(11)−Pt−N(2) = 81.46(18)° for **4a** and C(1)−Pt−N(1) = 84.23(13)° for **9c**).

Conclusions. In conclusion, compound [$PtPh_2(SMe_2)_2$], although less reactive than [$Pt_2Me_4(\mu\text{-}SMe_2)_2$] toward intramolecular activation of C−X bonds, has been shown to be an excellent metal precursor for the synthesis of three different types of cyclometalated compounds. As previously reported for the chemistry of dimethylplatinum analogues,[3] a concerted mechanism, involving prior dissociation of the dimethylamino group of the intermediate **3**, is suggested for intramolecular C−X bond activation. As shown in Scheme 3, for X = Br platinum(IV) compound **5** is obtained upon coordination of the NMe_2 moiety, while for X = H, compound **4** is formed along with reductive elimination of benzene. The more drastic conditions required for activation of the C−Cl bond along with the vacant site in the coordination sphere of platinum facilitate the process leading to compounds **6**. As described for compound [$PtBrPh_2(PhCH_2NCHC_6H_4)(SMe_2)$],[16] the process consists of reductive elimination to form a biaryl coordinated through the imine to platinum(II), followed by C−H activation

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Compounds 3a, 4a, and 9c with Estimated Standard Deviations

compound **3a**		compound **4a**		compound **9c**	
Pt−C(12)	1.977(11)	Pt−C(11)	1.986(6)	Pt−C(1)	1.996(3)
Pt−C(18)	1.992(8)	Pt−C(12)	2.009(4)	Pt−Cl(1)	2.3980(9)
Pt−N(2)	2.145(8)	Pt−N(2)	2.016(4)	Pt−N(1)	2.071(3)
Pt−N(1)	2.178(8)	Pt−N(1)	2.139(6)	Pt−P(1)	2.2347(10)
C(12)−Pt−C(18)	88.2(4)	C(11)−Pt−C(12)	98.36(18)	C(1)−Pt−N(1)	84.23(13)
C(18)−Pt−N(2)	97.5(4)	C(11)−Pt−N(2)	81.46(18)	C(1)−Pt−P(1)	94.42(11)
C(12)−Pt−N(1)	93.0(3)	C(12)−Pt−N(1)	99.1(2)	N(1)−Pt−Cl(1)	86.04(8)
N(2)−Pt−N(1)	81.3(3)	N(2)−Pt−N(1)	81.0(2)	P(1)−Pt−Cl(1)	95.32(3)

Scheme 3



and reductive elimination of benzene to yield the final compound. The reactions of the obtained cyclometalated compounds with triphenylphosphine confirm the stability of both five- and seven-membered platinacycles.

Experimental Section

General Procedures. Microanalyses were performed at the Servei de Recursos Científics i Tècnics de la Universitat Rovira i Virgili. FAB-mass spectra were performed at the Servei d'Espectrometria de Masses de la Universitat de Barcelona in a VG-Quattro spectrometer with 3-nitrobenzyl alcohol matrix. ^{1}H, ^{13}C, ^{19}F, ^{31}P, and ^{195}Pt NMR spectra were recorded at the Unitat de RMN d'Alt Camp de la Universitat de Barcelona using Varian Gemini 200 (^{1}H, 200 MHz), Varian XL300FT (^{13}C, 75.4 MHz; ^{19}F, 282.2 MHz), Varian Mercury 400 (^{1}H−^{13}C ghsqc; ^{1}H, 400 MHz; ^{13}C, 100.6 MHz), and Bruker 250 (^{31}P, 101.25 MHz; ^{195}Pt, 54 MHz) spectrometers, and referenced to SiMe$_4$ (^{1}H, ^{13}C), CCl$_3$F (^{19}F), H$_3$PO$_4$ (^{31}P), and H$_2$PtCl$_6$ in D$_2$O (^{195}Pt). δ values are given in ppm and J values in Hz.

Preparation of the Compounds. Compounds [PtPh$_2$(SMe$_2$)$_2$] (**1**)[29] and **2a**−**d**[3] were prepared as reported.

[PtPh$_2$(Me$_2$NCH$_2$CH$_2$NCHC$_6$H$_5$)] (3a) was obtained from 0.100 g (2.1 × 10^{-4} mol) of [PtPh$_2$(SMe$_2$)$_2$] (**1**) and 0.037 g (2.1 × 10^{-4} mol) of ligand C$_6$H$_5$CHNCH$_2$CH$_2$NMe$_2$ (**1a**) in 25 mL of toluene. The mixture was stirred at room temperature for 4 h, the solvent was evaporated in vacuo, and the remaining

Table 2. Crystallographic and Refinement Data for Compounds 3a, 4a, and 9c

	3a	**4a**	**9c**
formula	$C_{23}H_{26}N_2Pt$	$C_{17}H_{20}N_2Pt$	$C_{35}H_{33}Cl_2N_2PPt{\cdot}0.5C_3H_6O_6OH_6O$
fw	525.55	447.44	807.63
temp, K	293(2)	293(2)	293(2)
wavelength, Å	0.71069	0.71069	0.71073
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a, Å	7.0430(10)	14.5590(10)	12.7770(10)
b, Å	19.0655(16)	7.7300(10)	13.3150(10)
c, Å	15.1942(15)	15.0750(10)	21.2780(10)
β, deg	92.377(11)	114.29(10)	98.953(10)
V, Å^3; Z	2038.5(4); 4	1546.4(2); 4	3575.8(4); 4
d(calcd), Mg/m^3	1.712	1.922	1.500
abs coeff, mm^{-1}	6.891	9.065	4.146
F(000)	1024	856	1600
rflns collctd/unique	16 358/2421	15 370/4381	40 579/11 442
no. of data/restraints/params	2421/0/235	4381/0/169	11 442/0/426
GOF on F^2	1.164	1.030	1.205
$R_1(I > 2\sigma(I))$	0.0366	0.0380	0.0435
wR_2 (all data)	0.1252	0.0964	0.0963
peak and hole, e·Å^{-3}	0.675 and −0.910	0.647 and −0.606	1.127 and −1,137

residue was treated with diethyl ether to yield a white solid. Yield: 70 mg (63%). Anal. Found: C, 52.9; H, 5.0; N, 5.1. Calc for $C_{23}H_{26}N_2Pt$: C, 52.56; H, 4.99; N, 5.33. FAB-MS, *m*/*z*: 525 [M], 448 [M − Ph], 371 [M − 2Ph].

[$PtPh_2${$Me_2NCH_2CH_2NCH(2,6\text{-}Cl_2C_6H_3)$}] (**3c**), **[$PtPh_2${$Me_2NCH_2CH_2NCH(2\text{-}ClC_6H_4)$}]** (**3d**), and **[$PtPh_2(Me_2NCH_2CH_2NCHC_6F_5)$]** (**3e**) were obtained as yellow solids using an analogous procedure from **2c**, **2d**, and **2e**, respectively. **3c**: Yield 70 mg (56%). Anal. Found: C, 46.8; H, 4.4; N, 4.6. Calc for $C_{23}H_{24}Cl_2N_2Pt$: C, 46.47; H, 4.07; N, 4.71. FAB-MS, *m*/*z*: 593 [M], 558 [M − Cl], 516 [M − Ph], 481 [M − Cl − Ph]. **3d**: Yield 75 mg (64%). Anal. Found: C, 49.4; H, 4.5; N, 4.9. Calc for $C_{23}H_{25}ClN_2Pt$: C, 49.33; H, 4.50; N, 5.00. FAB-MS, *m*/*z*: 524 [M − Cl], 370 [M − Cl − 2Ph]. **3e**: Yield 75 mg (64%). Anal. Found: C, 44.5; H, 3.7; N, 4.3. Calc for $C_{23}H_{21}F_5N_2Pt$: C, 44.88; H, 3.44; N, 4.55. FAB-MS, *m*/*z*: 615 [M]; 461 [M − 2Ph].

[$PtPh(Me_2NCH_2CH_2NCHC_6H_4)$] (**4a**) was obtained by refluxing during 6 h a toluene solution (20 mL) containing 0.040 g (7.6×10^{-5} mol) of compound **3a**. The solution was filtered to remove a metallic residue, the solvent was evaporated in vacuo, and the remaining residue was treated with diethyl ether to yield a dark orange solid, which was recrystallized in dichloromethane−hexane and dried in vacuo. Yield: 25 mg (73%). Anal. Found: C, 45.3; H, 4.5; N, 5.9. Calc for $C_{17}H_{20}N_2Pt$: C, 45.63; H, 4.51; N, 6.26. FAB-MS, *m*/*z*: 447 [M], 370 [M − Ph].

[$PtBrPh_2(Me_2NCH_2CH_2NCHC_6H_4)$] (**5b**) was obtained from 0.100 g (2.1×10^{-4} mol) of [$PtPh_2(SMe_2)_2$] (**1**) and 0.054 g (2.1×10^{-4} mol) of ligand $2\text{-}BrC_6H_4CHNCH_2CH_2NMe_2$ (**2b**) in 25 mL of toluene. The mixture was stirred at room temperature for 4 h, the solvent was evaporated in vacuo, and the remaining residue was treated with diethyl ether to yield a white solid. Yield: 80 mg (62%). Anal. Found: C, 45.5; H, 4.1; N, 4.6. Calc for $C_{23}H_{25}BrN_2Pt$: C, 45.70; H, 4.17; N, 4.63. FAB-MS, *m*/*z*: 524 [M − Br], 447 [M − Br − Ph], 370 [M − Br − 2Ph].

[$PtCl(Me_2NCH_2CH_2NCHC_6ClH_3C_6H_4)$] (**6c**) was obtained from 0.060 g (1.00×10^{-4} mol) of compound **3c** in refluxing toluene for 2 h. The solvent was evaporated in vacuo, and the remaining residue was treated with diethyl ether to yield a light yellow solid. Yield: 35 mg (67%). Anal. Found: C, 39.3; H, 3.6; N, 5.2. Calc for $C_{17}H_{18}Cl_2N_2Pt$: C, 39.55; H, 3.51; N, 5.43. FAB-MS, *m*/*z*: 515 [M], 480 [M − Cl].

[$PtCl(Me_2NCH_2CH_2NCHC_6H_4C_6H_4)$] (**6d**) was similarly prepared from 0.060 g (1.07×10^{-4} mol) of compound **3d**. Yield: 23 mg (44%). Anal. Found: C, 42.1; H, 4.1; N, 5.5. Calc for $C_{17}H_{19}ClN_2Pt$: C, 42.37; H, 3.97; N, 5.81. FAB-MS, *m*/*z*: 481 [M], 446 [M − Cl].

[$PtPh(Me_2NCH_2CH_2NCHC_6H_4)(PPh_3)$] (**7a**) was prepared from 52 mg (1.2×10^{-4} mol) of **4a** and an equimolar amount of phosphine (32 mg) in acetone. After continuous stirring, acetone was evaporated in vacuo, and the remaining residue was treated with diethyl ether to yield a white solid. Yield: 60 mg (69%). Anal. Found: C, 59.4; H, 5.4; N, 3.8. Calc for $C_{35}H_{35}N_2PPt$: C, 59.23; H, 4.97; N, 3.95. FAB-MS, *m*/*z*: 709 [M], 632 [M − Ph].

[$PtCl(Me_2NCH_2CH_2NCHC_6ClH_3C_6H_4)(PPh_3)$] (**9c**) and **[$PtCl(Me_2NCH_2CH_2NCHC_6H_4C_6H_4)(PPh_3)$]** (**9d**) were similarly prepared from 50 mg of **6c** or **6d** and an equimolecular amount of PPh_3. **9c**: Yield 40 mg (55%). Anal. Found: C, 53.6; H, 4.5; N, 3.6. Calc for $C_{35}H_{33}Cl_2N_2PPt$: C, 53.99; H, 4.27; N, 3.60. FAB-MS, *m*/*z*: 778 [M], 743 [M − Cl]. **9d**: Yield 35 mg (47%). Anal. Found: C, 56.1; H, 4.7; N, 3.9. Calc for $C_{35}H_{34}ClN_2PPt$: C, 56.49; H, 4.61; N, 3.76. FAB-MS, *m*/*z*: 708 [M − Cl].

[$PtCl(Me_2NCH_2CH_2NCHC_6ClH_3C_6H_4)(PPh_3)$] (**8c**) and **[$PtCl(Me_2NCH_2CH_2NCHC_6H_4C_6H_4)(PPh_3)$]** (**8d**) were characterized by NMR in solution: 10 mg of the corresponding compound **6** was dissolved in 0.7 mL of $CDCl_3$ in a NMR tube, and an equimolar amount of PPh_3 was added. ^1H and ^{31}P NMR spectra were taken immediately after. A similar procedure was followed to monitor by NMR the reaction of [$PtBr(Ph)_2(Me_2NCH_2CH_2NCHC_6H_4)$] (**5b**) with triphenylphosphine, and spectra were taken at regular times until no further changes were observed.

X-ray Structure Analysis (3a, 4a, and 9c). Prismatic crystals were selected and mounted on a MAR345 diffractometer with an image plate detector. Intensities were collected with graphite-monochromatized Mo Kα radiation. The structures were solved by direct methods using the SHELXS computer program[30] and refined by the full-matrix least-squares method, with the SHELXL97 computer program using 2421 (**3a**), 4381 (**4a**), and 11 442 (**9c**) reflections (very negative intensities were not assumed). Further details are given in Table 2.

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Supporting Information Available: Complete NMR data (^1H, ^{13}C, ^{19}F, ^{31}P, and ^{195}Pt) for compounds **3**, **4**, **5**, **6**, **7**, **8**, **9**, and **10**, Figure S1, and tables giving all bond lengths and angles, refined and calculated atomic coordinates, and anisotropic thermal parameters for **3a**, **4a**, and **9c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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