Synthesis of New Ketonyl Palladium(II) and Platinum(II) Complexes with Nitrogen-Donor Ligands. Crystal Structure of [Pt{$CH_2C(O)Me$}$_2$(bpy)]

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Complexes [MCl_2L_2] (M = Pd, Pt; L_2 = 2,2′-bipyridine (bpy) or $Me_2N(CH_2)_2NMe_2$ (tmeda)) react with ketones MeC(O)R (R = Me, Et) in the presence of bases (Ag_2O or M′OH (M′ = Na, K)) to give the new types of ketonyl palladium(II) and platinum(II) complexes [M{$CH_2C(O)R$}ClL_2] (M = Pd, L_2 = *N*,*N*′,*N*′,*N*′-tetramethylethylenediamine = tmeda; M = Pt, L_2 = 2,2′-bipyridine = bpy) and [Pt{$CH_2C(O)R$}$_2L_2$] (R = Me, Et, L_2 = bpy). Oxidative addition of chloroacetone on [Pt(dba)$_2$] in the presence of bpy also yields [Pt{$CH_2C(O)R$}ClL_2]. [Pd{$CH_2C(O)Me$}Cl(tmeda)] reacts with $PhNHNH_2$ in the presence of TlOTf (OTf = CF_3SO_3) to give the cyclometalated complex [Pd{$CH_2C(Me)$═$NNH(Ph)$}(tmeda)]OTf. The crystal structure of [Pt{$CH_2C(O)Me$}$_2$(bpy)] has been determined. The platinum atom is in a distorted square-planar environment. The strong trans influence of the acetonyl ligand promotes the lengthening of both Pt−N bonds (2.082(3) and 2.091(3) Å) with concomitant narrowing of the NPtN bond angle (78.89(13)°).

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Introduction

Metalated ketones are important reagents in organic synthesis.[1] Those with transition metals are of particular interest.[2] We have recently reported a new way to prepare functionalized ketones by a C−C coupling process involving aryl(ketonyl)gold(III) complexes.[3] We have reported the syntheses of acetonyl derivatives of gold(III) and thallium(III) through two different C−H bond-activation processes[3−11] and a carbacyclic ketonylaryl palladium(II) complex by proton abstraction from a 2-acetylarylpalladium(II) complex with a phosphorus ylide or NaOMe.[12]

The number of acetonyl complexes of palladium(II) and platinum(II) is rather limited. So far, only monoacetonyl complexes have been reported, including the cationic complex [Pt{$CH_2C(O)Me$}$(PPh_3)_3$]BF_4[13] and a few neutral derivatives of the type [M{$CH_2C(O)Me$}XL_2] (M = Pd, Pt) for which the anionic X ligand can be Cl,[14−18] Ph,[14,19] Me,[19,20] or cyclohexen-1-yl[21] while the neutral L ligands are always tertiary phosphines (PEt_3,[14,19] $PMePh_2$, $PEtPh_2$,[15] PPh_3,[13,16,17,19] or L_2 = dppe[20,21]). These complexes have been prepared (i) by oxidative addition of chloroacetone to Pd(0) or Pt(0) complexes,[18] (ii) by reacting acetone with hydroxo complexes[19−22] or with chloro complexes in the presence of Ag_2O[14] or KOH (with or without added 18-crown-6),[15] or (iii) by a water-induced reaction of a cyclohexyne complex of Pt(0) with acetone.[21] The oxaallyl complex [Pd{η^3-$CH_2C(O)Me$}$(CNMe)_2$]PF_6 has been postulated as a component of the mixture formed in the photochemical reaction between [$Pd_2(CNMe)_6$]$(PF_6)_2$ and $ClCH_2C(O)Me$.[23] Oxodimethylenemethane derivatives of the type [M{$CH_2C(O)CH_2$}$(PPh_3)_2$] (M = Pd, Pt) have also been reported.[24,25]

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The reactivity of acetonyl complexes is almost unexplored. Insertion of isocyanides into the Pd−C bond of *trans*-[Pd{CH$_2$C(O)Me}Cl(PPh$_3$)$_2$] has been reported to produce β-ketoenamine ligands σ-bonded to palladium.[17] A similar behavior has been found in the corresponding PhC(O)CH$_2$ derivative.[26] Other ketonylpalladium complexes have been reacted with CO, ethylene, and butadiene to lead to C−C bond formation at the α-carbon of the starting ketones.[27] Treatment of [Pd{CH$_2$C(O)Bu^t}Br(PPh$_3$)$_2$] with Bu^{t}OK lead to the ylide Ph$_3$P=CHC(O)Bu^t.[28]

The few acetonyl complexes characterized by X-ray diffraction methods are of Mn,[29] Co,[30−32] Au,[8,9,33] Rh,[34] Hg,[35,36] and Tl.[6,9] No crystal structure of any acetonyl Pd or Pt complex is available so far. The only reported CH$_2$C(O)R derivatives of Pd(II) or Pt(II) are *trans*-[Pd{CH$_2$C(O)Ph}Cl(PPh$_3$)$_2$] and *cis*-[Pd$_2${μ-CH$_2$C(O)Ph}$_2$(PPh$_3$)$_4$].[26] ^{31}P NMR data conclusively prove that while in the case of platinum *cis*-[Pt{CH$_2$C(O)Me}Cl(PR$_3$)] and both *cis*- and *trans*-[Pt{CH$_2$C(O)Me}R′(PR$_3$)$_2$][15,18] (R′ = Me, Ph) complexes can be prepared, only the *trans*-[Pd{CH$_2$C(O)Me}Cl(PR$_3$)$_2$][18] isomers have been isolated in the case of palladium, which is in accordance with the known tendency of phosphines to avoid coordinating trans to carbon-donor ligands in palladium complexes (*transphobia*).[37]

Here, we describe some new ketonyl and ketimine complexes including the first acetonyl complexes of Pd(II) and Pt(II) with nitrogen-donor ligands, the first diacetonyl Pt(II) complex, and the first crystal structure of an acetonylplatinum complex.

Experimental Section

All of the reactions were carried out in normal laboratory conditions. Technical-grade solvents were purified by standard procedures. Conductivities were measured on ca. 5 × 10^{-4} M acetone solutions. Melting points are uncorrected. Unless otherwise stated, NMR spectra were measured in CDCl$_3$ on a Varian Unity 300 spectrometer at room temperature. Chemical shifts (in ppm) are referenced to TMS (^{1}H and ^{13}C{^{1}H}). Mass spectra (FAB) were measured using 3-nitrobenzyl alcohol as the dispersing matrix. Complexes [Pt(dba)$_2$][38] and [PtCl$_2$(bpy)][39] were prepared by literature methods. [PdCl$_2$(tmeda)] (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) was prepared by refluxing an acetone (20 mL) suspension of PdCl$_2$ (0.79 g, 4.47 mmol) and tmeda (0.52 g, 4.47 mmol) for 3 h. After the resulting suspension was stirred overnight, it was filtered and the solid washed with acetone and diethyl ether to give [PdCl$_2$(tmeda)] (1.25 g, 95%) as a yellow solid.

Synthesis of [Pd{CH$_2$C(O)Me}Cl(tmeda)] (1). [PdCl$_2$(tmeda)] (200 mg, 0.68 mmol) and Ag$_2$O (157 mg, 0.68 mmol) were refluxed in acetone (20 mL) for 3 h. The resulting suspension was filtered through Celite, the solution concentrated to dryness, and the residue treated with dichloromethane (15 mL). The mixture was allowed to settle in the refrigerator for 1 h and filtered through Celite. The clear yellow solution was concentrated (to ca. 2 mL), and diethyl ether (20 mL) was added to precipitate **1** as a yellow solid. Yield: 180 mg, 84%. Mp: 150 °C (decomp). Anal. Calcd for C$_9$H$_{21}$ClN$_2$OPd: C, 34.30; H, 6.72; N, 8.89. Found: C, 34.45; H, 6.67; N, 8.46. ^{1}H NMR: δ 2.26 (s, 2H, PdC*H*$_2$), 2.56 (s, 3H, *Me*CO), 2.64 (s, 6H, N*Me*$_2$), 2.69 (s, 6H, N*Me*$_2$), 2.5−2.8 (m, CH$_2$N). ^{13}C{^{1}H} NMR: δ 24.54 (Pd*C*H$_2$), 30.74 (*Me*C(O)), 48.81 (N*Me*$_2$), 49.99 (N*Me*$_2$), 58.36 (N*C*H$_2$), 63.94 (N*C*H$_2$), 213.58 (*C*O). IR (cm^{-1}): ν(CO), 1632 (s); ν(PdCl), 318 (m).

Synthesis of [Pt{CH$_2$C(O)Me}Cl(bpy)] (2). Bpy (2,2′-bipyridine, 36 mg, 0.229 mmol) and chloroacetone (0.06 mL, 0.72 mmol) were successively added to a suspension of [Pt(dba)$_2$] (dba = dibenzylideneacetone, 150 mg, 0.226 mmol) in acetone under a nitrogen atmosphere. The resulting suspension was stirred at room temperature for 3.5 h and concentrated to dryness. The residue was extracted with dichloromethane (3 × 20 mL), and the combined extracts were filtered through anhydrous MgSO$_4$. The solution was concentrated to ca. 2 mL, and diethyl ether (20 mL) was added to precipitate **2** as a yellow solid. Yield: 43 mg, 43%. Mp: 230 °C (decomp). Anal. Calcd for C$_{13}$H$_{13}$ClN$_2$OPt: C, 35.18; H, 2.95; N, 6.31. Found: C, 34.89; H, 2.88; N, 6.18. ^{1}H NMR: δ 2.29 (s, 3H, *Me*, $^4J_{HPt}$ = 12.7 Hz), 3.39 (s, 2H, *C*H$_2$, $^2J_{HPt}$ = 109 Hz), 7.9−7.99 (m, 2H), 8.47−8.68 (m, 4H), 9.46−9.65 (m, 2H). ^{13}C{^{1}H} NMR: not soluble enough. IR (cm^{-1}): ν(CO), 1636 (s); ν(PtCl), 338 (m).

2 was also obtained (50% yield) when a mixture of equimolar amounts (ca. 0.5 mmol) of [PtCl$_2$(bpy)] and KOH was refluxed in acetone (20 mL) for 36 h. The resulting suspension was concentrated to dryness, the residue extracted with dichloromethane (3 × 20 mL) and filtered through anhydrous MgSO$_4$, the solution concentrated to ca.1 mL, and diethyl ether (20 mL) added.

Syntheses of [Pt{CH$_2$C(O)R}$_2$(bpy)] (R = Me (3), Et (4)). Complexes **3** and **4** were prepared by refluxing [PtCl$_2$(bpy)] (ca. 0.5 mmol) with an excess of NaOH (molar ratio 1:15) in acetone (20 mL) (**3**) or methylethyl ketone (15 mL) (**4**) for 4 h. The reaction mixtures were concentrated to dryness, the residues extracted with dichloromethane (3 × 20 mL), and the extracts filtered through anhydrous MgSO$_4$. The solutions were concentrated to ca. 1 mL, and diethyl ether (20 mL) was added to precipitate the complexes as orange (**3**) and yellow (**4**) solids. **3**: yield, 64%. Mp: 150 °C (decomp.). Anal. Calcd for C$_{16}$H$_{18}$N$_2$O$_2$Pt: C, 41.29; H, 3.90; N, 6.02. Found: C, 41.11; H, 3.89; N, 6.10. ^{1}H NMR (200 MHz): δ 2.23 (s, 6H, *Me*, $^3J_{HPt}$ = 19 Hz), 3.26 (s, 4H, C*H*$_2$, $^2J_{HPt}$ = 120 Hz), 7.57 (m, 2H), 7.99 (m, 4H), 9.96 (m, 2H). ^{13}C{^{1}H} NMR: δ 21.94 (*Me*), 30.37 (*C*H$_2$), 122.04 (*C*5, *C*6), 126.93 (*C*3, *C*8), 137.61 (*C*4, *C*7), 150.49 (*C*2, *C*9) 155.95 (*C*$_{ipso}$), 215.26 (s, *C*O). IR (cm^{-1}): ν(CO), 1648 (s). MS (FAB$^+$): *m*/*z* 465 (M$^+$, 13.3), 448 (M$^+$ − Me, 16), 408 (100, M$^+$ − CH$_2$C(O)Me), 365 (Pt(bpy)CH$_2$, 17.5), 351 (Pt(bpy), 49.4). **4**: yield, 56%. Mp: 210 °C (decomp). Anal. Calcd for C$_{18}$H$_{22}$N$_2$O$_2$Pt: C, 43.81; H, 4.49; N, 5.68. Found: C, 43.76; H, 4.41; N, 5.77. ^{1}H NMR (200 MHz): δ 1.06 (t, *Me*, 6H, $^3J_{HH}$

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Table 1. Crystal Data for Compound 3

mol formula	$C_{16}H_{18}N_2O_2Pt$
mol wt	465.41
source	liquid diffusion CH_2Cl_2/Et_2O
description	prism
color	orange
cryst syst	monoclinic
a, Å	9.0603(5)
b, Å	9.1866(4)
c, Å	18.2871(10)
β, deg	101.904(4)
V, Å^3	1489.4(1)
Z	4
radiation (*λ*, Å)	Mo Kα (0.710 73)
temperature, K	173(2)
monochromator	graphite
space group	$P2_1/n$
cryst size, mm	0.32 × 0.26 × 0.18
μ, mm^{-1}	9.427
abs corr	*ψ* scans
max transmission, %	0.99
min transmission, %	0.35
diffractometer type	Siemens P4
data collection method	*ω* scans
2*θ* range, min−max, deg	6.4−50.0
hkl limits	$-10 < h < 10$
	$-10 < k < 10$
	$0 < l < 21$
no. of reflns measd	5219
no. of indep reflns	2617
R_{int}	0,034
R1[a]	0.0269
wR2[b]	0.0413

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ for reflections with $I > 2\sigma(I)$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{0.5}$ for all reflections; $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $P = (2F_c^2 + F_o^2)/3$ and *a* and *b* are constants set by the program.

= 7.4 Hz), 2.57 (q, MeCH_2, 4H, $^3J_{HH}$ = 7.5 Hz), 3.26 (s, CH_2, 4H, $^2J_{HPt}$ = 116 Hz), 7.57 (m, 2H), 7.97 (m, 4H), 9.79 (m, 2H). $^{13}C\{^1H\}$ NMR: *δ* 9.53 (s, *Me*), 20.45 (s, *C*H_2), 35.56 (s, *C*H_2Pt), 121.91 (*C*5, *C*6), 126.95 (*C*3, *C*8), 137.47 (*C*4, *C*7), 150.72 (*C*2, *C*9), 156.03 (C_{ipso}), 218.29 (s, *C*O). IR (cm^{-1}): *ν*(CO), 1642 (s).

X-ray Structure Determination of 3. A crystal of **3** was mounted in inert oil on a glass fiber and transferred to the diffractometer (Siemens P4 with LT2 low-temperature attachment) as summarized in Table 1. Unit cell parameters were determined from a least-squares fit of 73 accurately centered reflections (9.2° < 2*θ* < 25.0°). The structure was solved by direct methods and refined anisotropically on F^2 (program SHELXL-93).[40] Hydrogen atoms were included using a riding model or as rigid methyl groups. The final *R*(*F*) value was 0.0198 for 2225 observed reflections ($I > 2\sigma(I)$) and 192 parameters. The weighting scheme was $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $3P = (2F_c^2 + F_o^2)$, and *a* and *b* are constants adjusted by the program. Maximum $\Delta/\sigma = 0.001$, maximum $\Delta\rho = 1.16$ e Å^{-3}.

The programs use the neutral-atom scattering factors, *Δf′* and *Δf″* and absorption coefficients from ref 41.

Synthesis of [Pd{CH$_2$C(Me)=NNH(Ph)}(tmeda)]OTf (5). Phenylhydrazine (21 mg, 0.19 mmol) and TlOTf (OTf = CF_3SO_3, 67 mg, 0.19 mmol) were added to a solution of **1** (60 mg, 0.19 mmol) in dichloromethane (15 mL). The resulting suspension was stirred for 2 h at room temperature and filtered through Celite. The solution was concentrated (ca. 1 cm^3), and diethyl ether was added to give **5** as a yellow solid. Yield: 75 mg, 76%. Mp: 146 °C (decomp). Anal. Calcd for $C_{16}H_{27}F_3N_4O_3PdS$: C, 37.04; H, 5.25; N, 10.80; S, 6.18.

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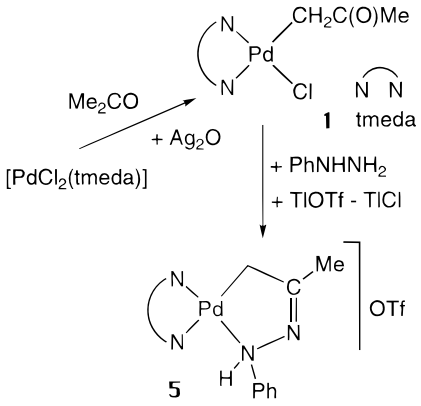
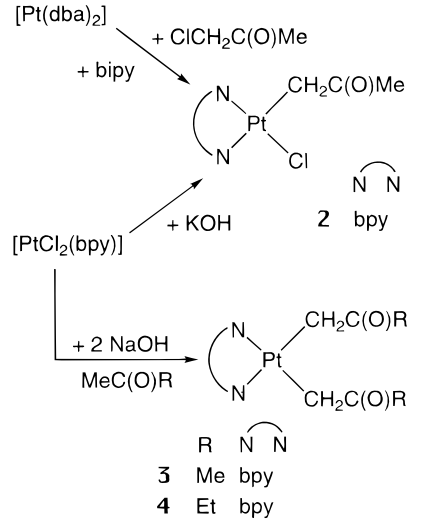
Scheme 1



Scheme 2



Found: C, 37.24; H, 5.23; N, 10.15; S, 6.01. Λ_M = 94 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR: *δ* 1.59 (s, 3H, *Me*C), 2.07 (s, 3H, *Me*N), 2.56 (s, 3H, *Me*N), 2.67 (s, 3H, N*Me*), 2.79 (s, 3H, N*Me*), 2.0−3.4 (multiplets, CH_2N and CH_2Pd), 7−7.6 (m, 5H, *Ph*), 9.31 (s, br, 1H, N*H*). $^{13}C\{^1H\}$ NMR: *δ* 17.63 (*Me*CN), 42.08 (*C*H_2Pd), 46.39, 49.64, 51.15, 52.82 (*Me*N), 58.88, 62.12 (*C*H_2N), 123.96, 127.96, 129.44 (*Ph*),145.54 (C_{ipso}), 180.13 (*C*=N). IR (cm^{-1}): *ν*(NH), 3150 (s).

Results and Discussion

Synthesis of Complexes. Mono- and diketonyl complexes [M{CH$_2$C(O)R}$_x$Cl$_{2-x}$L$_2$] (*x* = 1, R = Me, M = Pd, L$_2$ = tmeda (**1**); *x* = 1, R = Me, M = Pt, L$_2$ = bpy (**2**); *x* = 2, M = Pt, L$_2$ = bpy, R = Me (**3**), Et (**4**)] have been prepared in moderate to good yields by refluxing mixtures of the corresponding [MCl$_2$L$_2$] complexes and Ag$_2$O, NaOH, or KOH in the corresponding MeC(O)R ketone (see Schemes 1 and 2) according to procedures previously described.[14,15] None of these reactions proceed at room temperature, probably due to the insolubility of the starting metal complexes. The complex [PdCl$_2$(bpy)] does not react with Ag$_2$O in refluxing acetone while it does with NaOH or KOH, although mixtures of products, which could not be separated, were obtained. In the case of platinum, even when using a strict equimolar mixture of [PtCl$_2$(bpy)] and KOH in order to get the monoacetonyl complex **2**, the formation of a small amount of the diacetonyl derivative **3** cannot be avoided, and although complex **2** was

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analytically pure, the presence of **3** was detected in the ^{1}H NMR spectrum. Pure complex **2** can be obtained by the oxidative addition of chloroacetone to [Pt(dba)$_2$] (dba = dibenzylideneacetone) in the presence of added bpy at room temperature. The method had been reported previously.[17,18] An attempt to obtain complex **2** by the metathesis reaction of [PtCl$_2$(bpy)] with [Pt(CH$_2$COMe)$_2$(bpy)] failed, and the starting materials were recovered.

In the reactions of [PdCl$_2$(tmeda)] with basic compounds, we observed the opposite behavior with respect to the platinum case discussed above. In fact, not only can the monoacetonyl complex **1** be obtained in the presence of a large excess of Ag$_2$O (15:1), but furthermore we have not been able to prepare the diacetonyl complex after many different attempts, including using excess NaOH or KOH with prolonged refluxing.

Hydroxo complexes of palladium and platinum are strong bases and are known to react with somewhat acidic RH substrates such as MeNO$_2$, PhC≡CH, *p*-cresol, or even acetone to give the corresponding [M]R (R = nitromethylene, phenylethynyl, *p*-cresolato, or acetonyl) complexes.[14,15,19] Thus, it is not surprising that the reactions of chloro complexes of platinum bearing phosphine ligands with KOH (or NaOH) and acetone to give acetonyl derivatives have been thought to occur through the intermediacy of the corresponding hydroxo complexes, which, in a few cases, have even been isolated.[15] However, we have conclusively proved that this is not the case when [PtCl$_2$(bpy)] is used. In fact, while [Pt{CH$_2$C(O)Me}$_2$(bpy)] was obtained after refluxing [PtCl$_2$(bpy)] and NaOH in acetone for 4 h, [Pt(OH)$_2$(bpy)] was recovered unchanged after refluxing it in the same solvent for 5 h. We assume that in our case the acetonyl ligands—generated in situ on deprotonation of the ketone by the base—replace one or both chloro ligands from the starting complex with formation of the desired complexes **2** or **3** along with KCl or NaCl, respectively.

Reactions of Acetonyl Complexes. Complex **1** reacts with phenylhydrazine in the presence of TlOTf (OTf = CF$_3$SO$_3$) to give the cyclometalated complex [Pd{CH$_2$C(Me)═NNH(Ph)}(tmeda)]OTf (**5**) in good yield (see Scheme 2). Elimination of the chloro ligand as insoluble TlCl results in coordination of the hydrazine, condensation, and coordination of one of the nitrogen-donor atoms to give a five-membered ring; the whole process rapidly occurs at room temperature. Complex **3** is recovered unchanged after stirring for 2−24 h with dichloromethane solutions of aniline, *para*-methoxyaniline, or phenylhydrazine.

Structure of Complexes. Crystal Structure of [Pt{CH$_2$C(O)Me}$_2$(bpy)] (3) (See Table 1 and Figure 1). The platinum atom is in a distorted square-planar environment with Pt, C(1), C(4), N(1), and N(2) lying in a plane (mean deviation 0.017 Å). The Pt−N bond distances in complex **3** (2.082(3) and 2.091(4) Å) are longer than those found for other neutral complexes of the type [PtX$_2$(bpy)] (2.001 Å (X = Cl)[42] or 2.029 Å (X = I)[43]) but similar to those found when the X ligands are carbon donors (2.090[44]−2.145[45] Å), in agreement with the larger trans influence of these ligands. The Pt−C bond distances in **3** (2.088(4) Å) are longer than those found for other Pt−alkyl (1.969−2.038 Å)[45] bond distances but only marginally longer with respect to those containing, like in **3**, the Pt−CH$_2$C(sp^2) moiety (2.067 Å).[46] The NPtN bond angle in **3** (78.89(13)°) differs from the ideal value for square-planar coordination, which could be attributed not only to the small bite of the bpy ligand but also to the lengthening of the N−Pt−N bond distances (see above), causing concomitant narrowing of this angle keeping the N−N distance constant.

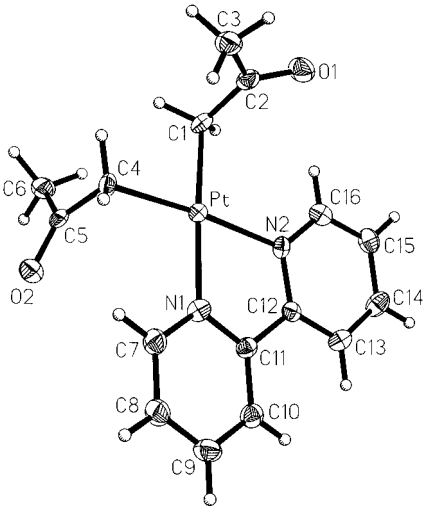

Figure 1. ORTEP plot of **3** with 50% probability ellipsoids and the labeling scheme. Selected bond lengths (Å) and angles (deg): Pt−C(4), 2.088(4); Pt−N(1), 2.082(3); Pt−N(2), 2.091(3); Pt−C(1), 2.088(4); C(4)−Pt−N(1), 96.0(2); N(1)−Pt−N(2), 78.89(13); C(4)−Pt−C(1), 89.1(2); N(2)−Pt−C(1), 95.94(14).

The ^{1}H and ^{13}C{^{1}H} NMR spectra of all these complexes show the expected resonances (see Experimental Section). In the ketonyl platinum complexes **2**−**4**, the singlet resonance with ^{195}Pt satellites corresponding to the CH$_2$ group appears in the 3.26−3.28 ppm region with $^2J_{PtH}$ coupling constants ranging from 108 (**2**) to 120 (**3**) Hz. It should be noticed that these resonances are shifted downfield ($\Delta\delta$ from 0.5 to 1.1 ppm) and the $^2J_{HPt}$ coupling constants are considerably larger (ΔJ_{PtH} from 10 to 52 Hz) than those in the analogous phosphine derivatives.[18,19] Both facts can be understood in terms of the higher electronegativity of the trans-donor atoms in our complexes.

In complex **5**, the presence of a chiral nitrogen center makes both of the methyl substituents at each NMe$_2$ group inequivalent, and correspondingly, four singlet resonances are observed for these methyl groups in the ^{1}H and ^{13}C NMR spectra. An acetone solution of **5** shows molar conductivity corresponding to a 1:1 electrolyte (94 Ω^{-1} cm^2 mol^{-1}), while complexes **1**−**4** are nonconducting in acetone.

The solid-state IR spectra of the ketonyl complexes show a strong absorption assignable to the ν(CO)

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stretching mode in the same region found for other ketonyl complexes.[16,18,19] The chloro complexes **1** and **2** also show the corresponding ν(MCl) absorptions 318 and 338 cm^{-1}, respectively. In the IR spectrum of the ketimine complex **5**, the band corresponding to ν(NH) appears at 3150 cm^{-1}. Those corresponding to δ(CNH), ν(C═N), and $\nu(CC)_{Ph}$ appear in a narrow range (at 1652 (m), 1602 (s), and 1560 (w) cm^{-1}), preventing their assignment.

Conclusions

The first ketonyl complexes containing nitrogen-donor ligands $[M\{CH_2C(O)R\}ClL_2]$ (M = Pd, Pt) and $[M\{CH_2C(O)R\}_2L_2]$ (M = Pt) have been prepared by reacting $[MCl_2L_2]$ complexes and the corresponding ketones in the presence of different bases (Ag_2O, NaOH, or KOH) or by the oxidative addition of chloroacetone on $[Pt(dba)_2]$ in the presence of added bpy. Different reaction trends have been found for palladium and platinum. While the diacetonyl complex of palladium could not be synthesized, the diacetonylplatinum complex formed readily, even during attempts to prepare the corresponding monoacetonyl derivative. The latter complex could only be obtained spectroscopically pure by oxidative addition of chloroacetone on $[Pt(dba)_2]$ in the presence of added bpy. On the other hand, while the acetonylpalladium complex reacts smoothly with phenylhydrazine to give the cyclometalated ketimine complex $[Pd\{CH_2C(Me)═NNH(Ph)\}(tmeda)]OTf$, no reaction (at room temperature) or decomposition (under heating) is observed for the diacetonylplatinum complex and phenylhydrazine or different amines.

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Supporting Information Available: An X-ray crystallographic file, in CIF format, for compound **3** is available through the Internet only. Access information is given on any current masthead page.

Note Added in Proof: The synthesis of complex **2** (by reacting *cis*-$[PtCl_2(NCMe)_2]$ with bpy for 15 days. Yield: 21%) and its crystal structure have been recently reported.[47]

OM971028V

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