Cyclometalated Complexes of Palladium(II) and Platinum(II) with *N*-Benzyl- and *N*-(Phenylethyl)-α-Benzoylbenzylideneamine. Delocalization in the Cyclometalated Ring as a Driving Force for the Orthometalation

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The cyclometalation of *N*-benzyl- and *N*-(phenylethyl)-α-benzoylbenzylideneamines with Pd(II) and Pt(II) salts has been studied. The structures of the Pt derivatives are very similar to those of the corresponding Pd complexes. The *endo* five-membered metallocycle, involving the less activated aromatic rings, is formed in all cases, regardless of the solvent used. The structures of the complexes are based on their IR and ^1H and ^{13}C NMR data. They were confirmed by X-ray studies of $[Pt(C_6H_4(C_6H_5C{=}O)C{=}N{-}CH_2C_6H_5)(\mu\text{-}OAc)]_2$ and $[Pd(C_6H_4(C_6H_5C{=}O)C{=}N{-}CH(Me)C_6H_5)(O{=}SMe_2)Cl]$. The first crystallizes in the centrosymmetric group $P\bar{1}$ with unit cell parameters a = 11.371 (2) Å, b = 12.074(2) Å c = 11.149(3) Å, α = 79.35(2)°, β = 89.50(3)°, γ = 77.94(2)°, V = 2270(1) Å^3, ρ(calcd) = 1.750 g cm^{-3}, and R = 0.042. The crystal structure of the second complex obtained by crystallization of $[Pd(C_6H_4(C_6H_5C{=}O)C{=}N{-}CH(Me)C_6H_5)(\mu\text{-}Cl)]_2$ from DMSO is the first reported DMSO O-bonded cyclometalated complex. The complex crystallizes in the orthorhombic system, with Z = 8, in the spatial group *Pbcn* with unit cell parameters a = 17.975(3) Å, b = 16.215(3) Å, c = 15.973(3) Å, V = 4656(3) Å^3, ρ(calcd) = 1.519 g cm^{-3}, and R = 0.038. From these and other previously studied X-ray crystallographic data and by taking into account the chemical shift of the carbon atoms remaining to the cyclometalated rings, a strong delocalization into the metalated ring can be proposed, which suggests that it could be one of the main driving forces to the preferred formation of *endo* metallocycles.

Introduction

In the intramolecular activation of C-H bonds, palladium(II) has been historically classified as a typical electrophile,[1-5] which was concluded from studies of enforced regioselectivity. Thus, cyclometalation of substituted azobenzenes[2,3] and 4-methyl-4′-nitrodibenzyl sulfide[4] took place on the electron-rich rings. Though deviations to this rule have been found, they were imputed to the solvent nature. Thus, the regioselectivity observed for cyclometalation of bifunctional dibenzylamines with $[Pd(OAc)_2]_3$ in $CHCl_3$ agrees with the electrophilic properties assigned to the reagent—cyclopalladation is aimed at the electron-rich aromatic ring—whereas it is the opposite in AcOH—the electron-poor aromatic ring is metalated—which was explained by assuming a nucleophilic character of the reagent in this solvent.[6,7] The *N*-benzylideneamines have been used as starting products to prepare *endo* and *exo* metallocycles.[8] The results obtained in these studies indicate that formation of *endo* complexes is usually preferred regardless of the solvent used, but the reasons for this preference are not well established. A possible explanation could be the aromatic character of the five-membered ring of the *endo* complexes (which involves the two conjugated double bonds (C=N—C=C) and the filled palladium d orbitals of appropriate symmetry), which was proposed by Crociani et al.[9] in order to explain the IR spectra of endocyclic complexes. Nevertheless, Albert et al.[8] have recently found that the C=N bond lengths of four exocyclic and endocyclic derivatives of *N*-benzylidenebenzylamines are identical and so the possibility that only the *endo* complexes were aromatic was excluded. Nevertheless these complexes exhibit many structural differences able to affect the C=N bond length, which put in question the validity of the deduced conclusion. We herein report the results obtained in the orthometalation with Pd(II) and Pt(II) salts of α-benzoylbenzylideneamines derived from

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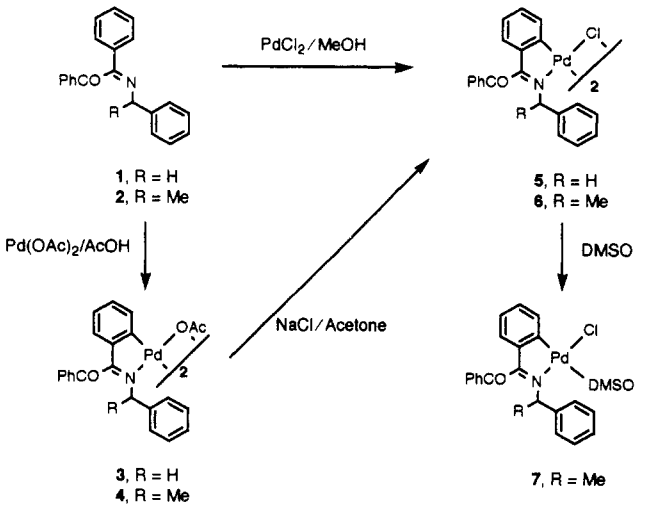
Scheme I



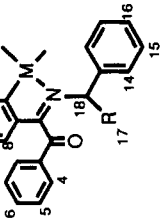
benzylamine, **1** (BNA), and phenylethylamine, **2** (PEA). This study has been carried out to obtain additional information about the reasons for the preferred formation of the *endo* complexes in cyclopalladation of *N*-benzylbenzylideneamines and to check if the same tendency is present in the less studied cycloplatination. On the other hand, we are also interested in comparing the antitumor activity of the Pt complexes (which is presently underway) with that of the palladium ones, which has been recently described by us, for two diastereoisomeric cyclopalladated complexes derived from benzoylbenzylideneamines.[10]

Results and Discussion

Synthesis of the Complexes. Cyclometalation of benzoylbenzylideneamines derived from benzylamine (BNA) and phenylethylamine (PEA) could lead to different *endo* and *exo* palladium(II) imine complexes, depending on the ring (less or more activated, respectively) where the reaction takes place. Treatment of equimolar amounts of $[Pd(OAc)_2]_3$ with BNA (**1**) in AcOH, afforded the corresponding acetate-bridged complex **3** (Scheme I), while the use of PEA (**2**) as ligand yielded **4**, whose IR spectrum suggests an acetate-bridged dimer structure but whose ^1H NMR spectrum indicates the existence of different isomers (see Experimental Section) such that it is not possible to solve (Scheme I). However the reaction of **1** and **2** with $PdCl_2$ in MeOH yielded the chloro-bridged complexes **5** and **6**, respectively. **5** can also be obtained by metathesis of the acetate-bridged complex **3** with NaCl in acetone, while under the same conditions, the mixture **4** evolved into **6**. The crystallization of **6** in dimethyl sulfoxide (DMSO) undergoes bridge-splitting to give complex [Pd(PEA)(DMSO)Cl] (**7**).

Formation of the corresponding chloro-bridged cycloplatinated complexes was not possible by using standard methods, such as K_2PtCl_4 in MeOH or $EtOH/H_2O$[11] or in dioxane/H_2O.[12] So, in aqueous medium, all attempts to orthoplatinate the ligands yielded the coordination complexes of the amines, resulting in the hydrolysis of the ligands (readily hydrolyzable as a consequence of the withdrawing effect of the $CO-C_6H_5$ group). The orthoplatinated complexes **8** and **9** could only be obtained by

Table I. ^1H NMR Data (ppm) for Palladium and Platinum Complexes[a]



	1	3 (M = Pd)[b]	10 (M = Pt)[c]	5 (M = Pd)	8 (M = Pt)	2	6 (M = Pd)	9 (M = Pt)
H4	7.95, m, 2H			7.86, m, 2H	7.81, m, 2H	7.86, m, 2H	7.93, m, 2H	7.87, m, 2H
H5	7.47, m, 2H			7.61, m, 2H	7.58, m, 2H	7.40, m, 2H	7.66, m, 2H	7.59, m, 2H
H6	7.62, m, 1H			7.80, m, 1H	7.77, m, 1H	7.57, m, 1H	7.79, m, 1H	7.76, m, 1H
H8	7.77, m, 2H			6.75, d (7.6), 1H	6.88, ddd (0.4, 1.1, 7.7), 1H	7.77, m, 2H	6.71, d (6.9), 1H	6.56, d(7.2), 1H
H9				6.96, t (7.6), 1H	7.07, dt (1.1, 7.7), 1H		6.95, t (6.9), 1H	6.79, t (7.2), 1H
H10				7.09, t (7.6), 1H	7.26, m, 1H		7.07, t (6.9), 1H	7.05, dt, (0.9, 7.2), 1H
H11	7.39–7.16, m			7.70, d (7.6), 1H	8.23,[d] ddd (0.4, 1.1, 7.7), 1H	7.30–7.16, m	n.o.	8.25, dd[e] (0.9, 7.2), 1H
H14								
H15				7.35–7.16, s br	7.28–7.15, m		7.60–7.20, m	7.40–6.90, m
H16								
H18	4.65, s, 2H	4.55, s br, 3H	4.76, s br, 3H	4.64, m, 2H	5.32 and 4.91[e] (14.3), 2H	1.50, d (6.4), 3H	1.70, d (6.4), 3H	1.79, s, 3H
Me[f]		2.07, s, 3H	2.10, s, 3H			4.63, q (6.4), 1H	4.69, q (6.4), 1H	6.25, s br, 1H

[a] The numbers in parentheses correspond to $J(^1H-^1H)$ in Hz. m = multiplet; s = singlet; s br = singlet broadened; q = quartet; n.o. = not observed. [b] Broadened unresolved pattern in aromatic zone at 6.80–7.60 ppm for **3**. [c] Broadened unresolved pattern in aromatic zone at 6.65–7.55 ppm for **10**. [d] $J(^{195}Pt-^1H) = 41.6$ Hz. [e] AB System; $J(^{195}Pt-^1H) = 27.7$ and 44.8 Hz. [f] Corresponding to acetate group. [g] $J(^{195}Pt-^1H) = 40.0$ Hz.

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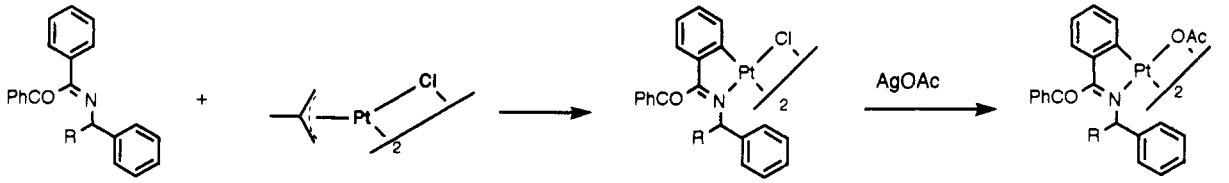
Scheme II



1, R = H
2, R = Me

8, R = H
9, R = Me

10, R = H
11, R = Me

starting from $[Pt(\mu\text{-}Cl)(\eta^3\text{-}C_4H_7)]_2$[13] (Scheme II), with $CHCl_3$ (but not acetone) as the solvent. The chloro-bridged complexes **8** and **9** were respectively converted to the acetate-bridged analogues **10** (L = BNA) and **11** (L = PEA) by treatment with silver acetate in $CHCl_3$. Similarly to palladium complex **4**, the ^1H NMR spectrum of complex **11** revealed that it was a mixture of isomers which could not be purified.

Characterization of the Complexes. All new complexes are air-stable solids. The acetate dimers, **3**, **4** (orange), **10**, and **11** (deep red), are soluble in most organic solvents, whereas, the chlorine derivatives, **5**, **6** (yellow), **8**, and **9** (green), are slightly soluble in organic solvents, but soluble in DMSO and DMF.

Comparison of the IR data for the ligands[14] and complexes **1**–**11** shows that the C=O stretching modes are scarcely modified, whereas, the C=N stretching frequency is lower in the complexes, proving association through nitrogen. For complex **7**, IR spectroscopy is also useful for the DMSO coordination position assignment. Studies carried out on different complexes with sulfoxides as ligands[15] conclude that an increase in the observed value for the S=O stretching mode (which in free DMSO appeared at 1055 cm^{-1}) indicates coordination via the sulfur atom, whereas if it takes place through the sulfinyl oxygen, a decrease of the normal value is observed. For complex **7**, the S=O stretching mode appears at 953 cm^{-1}, *ca.* 100 cm^{-1} lower than that corresponding to free DMSO, which indicates that O-coordination is taking place.[16]

The ^1H NMR data for **1** and **2** and their orthopalladated (**3**, **5**, and **6**) and orthoplatinated (**8**–**10**) complexes are depicted in Table I. Spectra were assigned on the basis of chemical shift and spin–spin coupling information and were confirmed by selective proton decoupling. The *trans* arrangement of the ligands in the acetates **3** and **10** is inferred from the fact that the acetate-bridge methyl groups appear as only one singlet at 2.07 and 2.10 ppm, respectively (the *cis* arrangement of the ligands in the complex shows the methyl groups appearing as two singlets). On the other hand, the fact that these complexes show a broadened unresolved pattern in the aromatic region could be explained by assuming an open-book shape (with mutual interaction of the aromatic moieties of the ligands), which is supported by X-ray data of similar complexes.[17]

Comparison of the ^1H NMR spectra of complexes **5** and **6**, whose aromatic regions appear as well-resolved patterns, with those of the ligands clarifies several structural aspects. The small differences observed in the aromatic ring proton signals joined to CO and CH or CH_2 groups suggest both that the carbonyl group is not associated with the palladium atom and that these rings are not involved in orthometalation. The large variation observed for the chemical shift of protons H8–H11, remaining to the phenyl ring joined to the C=N group, evidences the Pd—N association as well as cyclometalation through the benzylideneamine ring. Shielding observed for H9 could be due primarily to the flow of charge from the electron-rich (d^8) metal atom into the aromatic ring (π-back-bonding).[18] The strong shielding effect at H8 must be a consequence of the change in the spatial arrangement of the COC_6H_5 group of the cyclometalated complexes, with respect to that exhbited by the ligand. However, H11 is strongly deshielded after cyclopalladation despite the retrodonating character of the metal, which could be a consequence of the steric effect of the metalated substituent at C12.

The NMR parameters of platinated complexes **8** and **9** are very similar to those of their corresponding palladated complexes. The main difference is the larger chemical shift observed for H11 in the platinum complexes, which demonstrates that platinum has a stronger deshielding effect than the palladium on the *ortho* positions.

The signals corresponding to H11 in Pt complexes **8** and **9** show the splitting due to their coupling with the metal [$^3J(^{195}Pt\text{–}^1H)$ of *ca.* 40 Hz] which distinguishes between H8 and H11.

The ^{13}C NMR parameters of ligands **1** and **2**[19] and those of their palladium and platinum complexes are shown in Table II. Spectra were assigned by heteronuclear 2D correlation spectroscopy[20] and quaternary carbon atoms by the heteronuclear NOE.[21] The comparison between the spectra of the ligands and complexes reveals that the main differences are observed in the signals corresponding to the carbons C7–C12 as well as those of C1 and C2 which demonstrates that cyclometalation takes place on the phenyl group joined to the imine carbon and confirms the structural assignment made from IR and ^1H NMR.

There are few papers about the influence of the metal on the carbon chemical shifts in orthopalladation reactions. When a Pd–C aliphatic bond is formed, a small deshielding ($\Delta\delta \simeq 5$ ppm)[22] is observed, which became larger in the case of a Pd–C aromatic bond ($\Delta\delta \simeq 18$ ppm),[22] probably due to the Pd–C back-bonding. This effect is substantially larger for azobenzene and benzylideneamine complexes, where $\Delta\delta$ is higher than 30 ppm. Certainly these differ-

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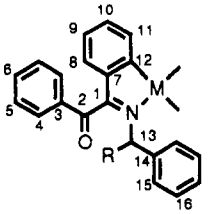
Table II. ^{13}C NMR Data for the Ligands and Palladium and Platinum Complexes (ppm)



	1	3	10	5	8	2	6	9
C1	166.6	181.1	182.8 J = 41.6	180.7	186.7 J = 93.9	164.4	179.9	185.2
C2	198.4	192.2	192.4 J = 77.6	192.8	192.4 J = 50.0	198.7	193.6	192.3
C3	134.2	133.8	133.9	133.1	133.6	134.9	133.3	132.6
C4,4′	129.0	130.5	129.2	129.7	129.2	129.3	129.6	128.8
C5,5′	128.8	129.4	129.2	129.3	129.7	129.0	129.5	129.1
C6	134.5	135.9	134.9	136.1	136.2	134.5	135.6	134.9
C7	134.8	146.4	145.4	145.7	144.6 J = 55.5	135.4	145.4	145.0
C8	128.3	128.2	n.o.	127.6	129.2	128.6	129.4	129.4
C9	127.6	124.3	123.0	124.2	124.6	127.5	124.3	124.4
C10	130.1	132.3	131.1 J = 39.8	130.4	133.0	130.8	131.3	133.0
C11	127.6	134.9	131.6 J = 44.2	136.8	133.2	127.5	136.2	133.3
C12	128.3	155.7	139.9 J = 1198.6	154.2	146.0 J = 1098.1	128.6	153.7	146.1
C13	138.7	n.o.	136.0	n.o.	136.6	144.5	136.3	137.7
C14,14′	127.1	128.2	128.2	128.2	128.1	126.6	129.0	128.4
C15,15′	128.0	128.2	127.4	128.2	127.3	128.3	128.8	127.9
C16	126.6	127.4	127.4	127.2	127.1	126.9	128.4	127.7
C17						24.6	17.9	18.1
C18	56.9	57.6	59.1	56.2	56.1	62.1	61.4	61.7
C19[a]		24.2	23.9					
C20[a]			183.9					

[a] Corresponding to acetate methyl group. $J(^{195}Pt-^{13}C)$ in Hz.

ences can be attributed to the different natures of the Pd–C bond or to the different steric effects of the ligands, and it can be reasonably accepted that the Pd–C back-bonding is responsible for the observed differences; as Pople's equation[23] indicates, an increase in M–C bond order due to the π-back-bonding increases the deshielding term, σ^{para}.

The spectra of cycloplatinated complexes **8–10** are very similar to those of their palladium analogues, which suggests that they have analogous structures. The most significant differences depending on the metal are observed in C1 and C12, both directly involved in the cyclometalated ring. A larger shielding is observed for C12, linked directly to the metal, in platinum derivatives (compare δ(C12) values in **8** and **9** with those in **5** and **6**, respectively), whereas these complexes exhibit a larger deshielding for C1. Both effects must be attributed to electronic perturbations due to the metal itself and therefore different for Pd and Pt.[24] On the other hand, the almost identical chemical shifts of C8, C9, and C10 (where the proximity effects are not possible) observed for both types of metallic complexes suggest that palladium and platinum have a similar electronic back-bonding effect. Finally the δ values observed for C1 in the Pd complexes are very similar in the acetate and chlorine derivatives, whereas in the case of the Pt complexes, there are significant differences depending on the bridge ligand (AcO^- or Cl^-). This fact could indicate that structural differences associated with the nature of the metal and/or the ligand, could exist. As they cannot be deduced from the NMR parameters, the study of some of these complexes by X-ray diffraction must be considered.

In a recent paper, two cyclopalladated complexes with acetate bridges [*N*-(4-methoxyphenyl)-α-benzoylbenzylideneamines (**12** and **12′**)][17] were reported, whose structures are very similar to that proposed for complex **3**. Therefore, comparison of the crystal structure of **12′** with that of the Pt complex **10** would demonstrate the influence of the metal on the structure of these acetates. On the other hand, the comparative study of the crystal structures of **6** and **9** would also give information about the same problem in the case of Cl-bridge complexes.

Crystallization of **10** was easily achieved from $CHCl_3$/MeOH, but starting from **6** we could only obtain suitable crystals when it was crystallized from DMSO. Crystal structure determination confirmed that bridge-splitting had occurred by DMSO to afford the corresponding mononuclear cyclopalladated complex **7** (Scheme I); the structural study of **7** was also interesting.

Crystal Structure of [Pd(C_6H_4(C_6H_5C=O)C=N—CH(Me)C_6H_5)(O=SMe_2)Cl], 7. The crystal structure is shown in Figure 1 together with the atomic numbering scheme. The structure consists of discrete molecules separated by van der Waals distances. The palladium atom is bonded to four atoms, C108, N101, Cl, and O2, in a quasi planar coordination with C108, N101, Cl, and O2 in a plane and Pd +0.017 Å out of this plane. The five-membered chelate ring has an envelope form, with C108, C103, C102, and N101 atoms in a plane, deviating from the mean plane passing through them by +0.004, −0.007, +0.007, and −0.004 Å, respectively; the palladium atom is out of this plane.

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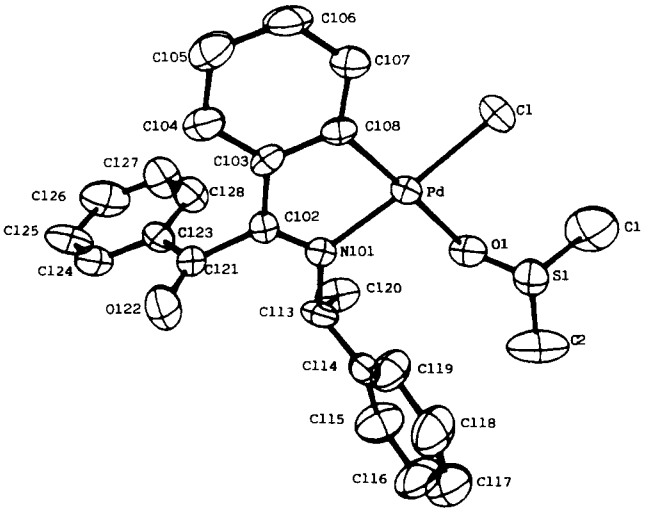

Figure 1. Molecular structure of **7** showing the atom numbering scheme. H atoms have been omitted for clarity.

Table III. Final Atomic Coordinates (×10⁴) and Thermal Parameters[a] for 7

atom	*x/a*	*y/b*	*z/c*	*B*(eq), Å²
Pd	29123(2)	38878(3)	19716(3)	2.55(2)
Cl	40940(9)	37233(11)	14607(11)	3.85(7)
O1	961(3)	4262(3)	4204(3)	4.48(24)
N101	1890(3)	4094(3)	2510(3)	2.62(20)
C102	1921(3)	4468(4)	3213(4)	2.59(24)
C103	2660(4)	4622(4)	3553(4)	2.88(25)
C104	2779(4)	4970(4)	4341(5)	3.70(32)
C105	3509(5)	5071(5)	4629(5)	4.39(37)
C106	4090(4)	4805(5)	4128(5)	4.51(37)
C107	3965(4)	4468(4)	3334(4)	3.42(30)
C108	3255(3)	4354(4)	3044(4)	2.67(24)
C113	1157(4)	3905(5)	2117(5)	3.70(31)
C114	1068(4)	2979(4)	1976(4)	3.36(28)
C115	1515(4)	2404(4)	2367(5)	4.32(34)
C116	1391(5)	1567(6)	2286(7)	5.58(49)
C117	837(5)	1278(6)	1778(7)	6.10(51)
C118	375(5)	1847(6)	1398(7)	6.47(50)
C119	496(5)	2680(6)	1488(6)	5.75(48)
C120	1082(5)	4430(5)	1322(6)	4.68(40)
C121	1254(3)	4741(4)	3721(4)	2.81(26)
O122	2485(3)	3400(3)	810(3)	3.77(21)
C123	1012(3)	5611(4)	3600(4)	3.00(26)
C124	431(4)	5925(5)	4081(5)	3.94(36)
C125	204(5)	6727(5)	3973(6)	5.19(42)
C126	557(6)	7216(6)	3385(8)	6.16(51)
C127	1119(5)	6919(5)	2908(6)	5.33(43)
C128	1353(5)	6108(5)	3020(5)	4.28(33)
SA[b]	2694(7)	2575(4)	543(6)	3.92(29)
SB[b]	2838(12)	2635(11)	360(18)	7.58(62)
C1	3345(7)	2736(7)	−361(7)	8.01(65)
C2	1925(8)	2264(10)	−86(12)	11.75(101)

[a] $B(\text{eq}) = (8\pi^2/3)\sum_{ij}U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$. [b] S atom in disordered position, occupancy factor equal to 0.56(3) in the first position.

Final positional and thermal parameters for all non-hydrogen atoms are listed in Table III, and bond distances and angles are summarized in Table IV.

The Pd–C108 distance [1.971(6) Å] is shorter than that predicted by addition of the covalent radii[25] (2.05 Å) but similar to those found for other cyclometalated complexes.[25,26] The Pd–N101 [2.057(5) Å] and Pd–Cl [2.291(2) Å] distances are similar to those observed in cyclometalated complexes[25,26] and $PdCl_2(DMSO)_2$,[27] respectively.

Table IV. Selected Bond Distances and Angles for 7

	Distances (Å)		
Pd–N101	2.057(5)	C104–C105	1.400(10)
Pd–C108	1.971(6)	C105–C106	1.385(11)
Pd–Cl	2.291(2)	C106–C107	1.400(9)
Pd–O1	2.159(4)	C107–C108	1.370(8)
N101–C102	1.278(7)	C103–C108	1.412(9)
C102–C103	1.456(8)	C121–O122	1.215(7)
C102–C121	1.514(8)	C121–C123	1.489(8)
C103–C104	1.397(8)		
	Angles (deg)		
Cl–Pd–O1	88.9(1)	Pd–N101–C102	113.8(4)
C108–Pd–Cl	93.7(2)	N101–C102–C103	116.8(5)
N101–Pd–O1	95.8(2)	C102–C103–C108	115.0(5)
N101–Pd–C108	81.6(2)	Pd–C108–C103	112.5(4)

As we can see in Figure 1, DMSO is O-bonded instead of S-bonded to Pd. There are only three reported examples of X-ray structures of O-bonded DMSO to Pd.[28–30] It has been suggested that small or highly charged metal ions favor coordination to sulfoxides *via* the O-bonding, whereas large or less highly charged metal ions tend to favor S-bonding. According to this assumption, DMSO should be S-bonded to Pd(II) unless there were steric reasons to prevent this,[31] in which case O-bonding would be observed.[32] Taking into account that complex **7** has no important steric interactions, the O-coordination exhibited by DMSO in this complex could not be easily explained. Although the single O–metal association must be stronger than the corresponding S–metal one, we think that one of the main reasons the sulfoxides prefer the S-bonding derives from the retrodonating capability of the metal, able to act on the empty 3d orbitals at the sulfinyl sulfur atom, reinforcing the S–metal bond, but unable to do the same on the oxygen. Therefore, in the cases where the retrodonation on sulfur was not possible, the O-bonding must be expected. This is the case of complex **7**, where the lone electron pair at the metal is involved in a strong back-donation on the aromatic ring, precluding the metal to act as donor to the sulfur. Similar situations can be expected in other cyclometalated complexes in which the metal can act as a retrodonating group on some appropiate substituent.[28–30] This is in agreement with the previously postulated assumption[28] that a transition from S- to O-bonded DMSO must take place when the π-acceptor capacity of the *trans* ligand is increased.

The Pd–O distance of 2.159(4) Å observed in **7** is longer than those of 2.061(9) and 2.065(10) Å reported for $[Pd(DMSO)_4][BF_4]_2\cdot DMSO$[30] and 2.024(2) Å reported for $[Pd(bpy)(DMSO)Cl][BF_4]_2$[28] (these complexes also exhibit the O-bonded DMSO). Despite the long and weak N···Pd dative bond involved in this last bipyridine complex a $d\pi$–$p\pi$-back-bonding has been suggested.[28] We proposed a similar interaction, but it is much more important in the case of **7**, due to the covalent nature of the Pd–C bond. This fact justifies the weakening of the Pd–O bond in **7** (with respect to that in the bipyridine complex) due to the *trans* effect of the Pd–C bond. The sulfur atom in DMSO has a disordered position.

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Table V. Final Atomic Coordinates (×10⁴, Pt × 10⁵) and Thermal Parameters[a] for 10

atom	x/a	y/b	z/c	B(eq), Å²	atom	x/a	y/b	z/c	B(eq), Å²
Pt1	17403(5)	17761(5)	16647(4)	2.92(2)	C205	3056(21)	−99(13)	5372(10)	5.76(96)
N101	3099(11)	537(9)	2065(9)	3.47(57)	C206	2050(19)	−398(17)	5020(10)	5.40(97)
C102	4186(17)	754(12)	1945(7)	3.81(70)	C207	1353(14)	334(11)	4395(8)	2.89(61)
C103	4158(14)	1914(12)	1486(8)	3.53(66)	C208	1669(13)	1373(14)	4045(9)	3.58(68)
C104	5261(15)	2349(14)	1339(12)	5.13(84)	O209	−429(8)	1678(9)	2992(7)	3.61(47)
C105	5058(21)	3435(18)	974(12)	6.50(114)	C210	−413(15)	912(12)	2498(10)	3.82(73)
C106	3939(17)	4162(14)	773(9)	5.34(82)	O211	389(8)	800(10)	2005(6)	3.66(49)
C107	2936(13)	3741(13)	944(10)	4.02(72)	C212	−1373(16)	304(17)	2536(13)	5.77(104)
C108	3015(15)	2575(12)	1339(9)	3.45(66)	C213	2127(15)	4574(14)	3042(11)	4.39(80)
O109	401(9)	3041(10)	1144(7)	4.09(49)	C214	1300(13)	5460(11)	3421(9)	2.87(58)
C110	−242(13)	3787(15)	1436(9)	3.61(71)	C215A[b]	358(46)	5084(43)	3890(33)	6.50(38)
O111	−76(10)	3906(8)	2204(7)	4.05(52)	C215B[b]	−53(34)	5576(31)	3541(23)	4.04(23)
C112	−1222(17)	4682(16)	960(11)	5.36(90)	C216A[b]	−753(34)	6417(31)	3916(24)	4.16(23)
C113	2879(21)	−482(15)	2570(14)	6.83(127)	C216B[b]	−337(45)	6189(41)	4273(31)	6.22(36)
C114	3788(15)	8309(13)	2442(11)	3.80(77)	C217A[b]	−79(39)	7190(35)	4005(25)	3.73(25)
C115	4462(15)	7567(15)	3080(12)	4.58(81)	C217B[b]	−447(68)	7371(66)	4130(49)	10.01(76)
C116	5100(22)	6555(17)	2972(18)	7.19(135)	C218A	640(22)	7512(20)	3555(15)	1.70(13)
C117	5151(20)	6247(16)	2235(22)	8.87(140)	C218B	1147(37)	7263(33)	3967(25)	4.94(26)
C118	4463(22)	6998(16)	1576(17)	7.93(141)	C219A	1787(25)	6429(23)	3537(18)	2.44(16)
C119	3774(16)	8079(14)	1709(12)	5.13(91)	C219B	1440(54)	6629(50)	3108(39)	9.54(50)
C121	5344(12)	−33(8)	2308(8)	2.17(51)	C221	3685(15)	3387(19)	4449(12)	5.42(99)
O122	5561(11)	−94(10)	3034(7)	4.67(58)	O222	3401(11)	3730(13)	5038(8)	6.57(82)
C123	6147(14)	−750(16)	1795(9)	4.35(80)	C223	5004(11)	3313(11)	4109(9)	2.82(58)
C124	7042(10)	−1578(11)	2176(12)	3.68(64)	C224	5256(17)	3047(15)	3399(8)	4.21(79)
C125	7803(15)	−2230(15)	1719(14)	5.55(93)	C225	8449(15)	3072(15)	3073(12)	5.91(89)
C126	7654(20)	−1986(17)	897(14)	6.19(118)	C226	7263(19)	3404(17)	3540(15)	5.78(110)
C127	6800(16)	−1137(14)	488(13)	4.91(88)	C227	6888(15)	3740(16)	4254(15)	5.59(102)
C128	6047(16)	−508(12)	942(10)	3.73(71)	C228	5810(16)	3706(11)	4551(9)	3.58(68)
Pt2	835(1)	2567(1)	3165(0)	2.74(2)	C1	766(20)	−1931(14)	324(13)	5.85(102)
N201	2086(12)	3388(11)	3450(8)	3.51(58)	Cl1	593(5)	9065(5)	932(4)	6.38(29)
C202	2819(12)	2820(10)	4055(9)	2.86(59)	Cl2	1045(7)	6652(5)	963(4)	7.63(34)
C203	2648(13)	1695(14)	4402(8)	3.19(61)	Cl3	7931(6)	1891(7)	277(4)	8.33(39)
C204	3315(18)	933(17)	5071(13)	5.63(108)					

[a] $B(\text{eq}) = (8\pi^2/3)\sum_{ij}U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$. [b] C215, C216, C217, C218, and C219 atoms in disordered position, occupancy factor equal to 0.5.

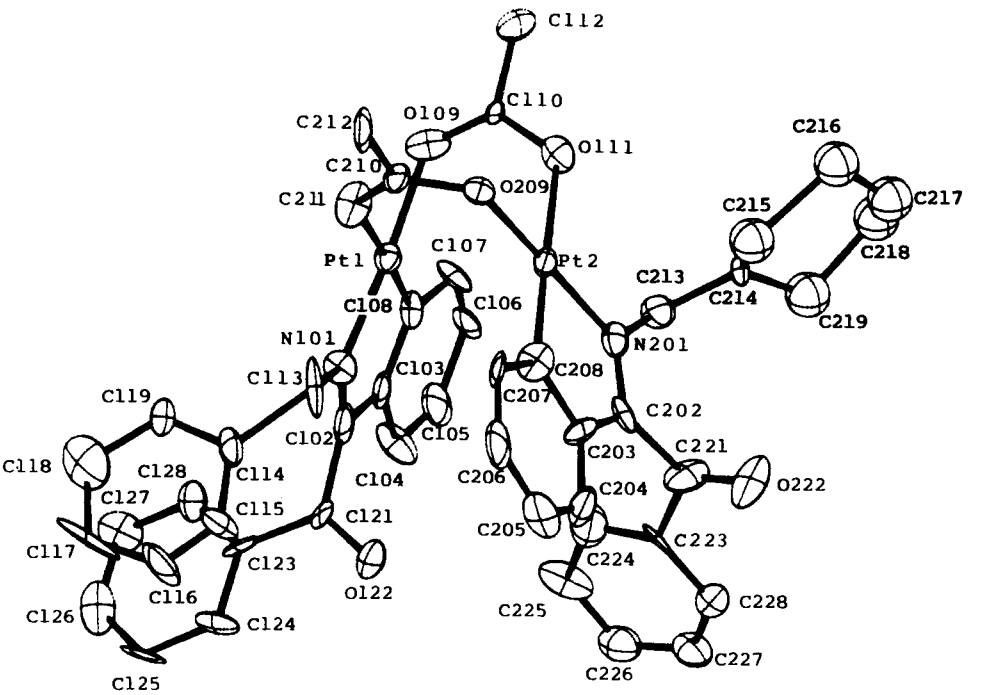


Figure 2. Molecular structure of **10** showing the atom numbering scheme. H atoms have been omitted for clarity.

Crystal Structure of [Pt(C_6H_4(C_6H_5C=O)C=N—$CH_2C_6H_5$)(μ-OAc)]₂, 10. The structure consists of discrete dimeric molecules without any symmetry element. Each platinum atom is bonded to four atoms—the nitrogen, the *ortho* carbon atom of the phenyl ring supporting the iminic carbon, and one oxygen atom from each of the two bridging acetates—in a distorted square-planar coordination with tetrahedral geometry. Two cyclometalated rings are planar, with C103 +0.017 Å and C202 +0.01 Å out of these planes, respectively.

Final positional and thermal parameters for all non-hydrogen atoms are listed in Table V, bond distances and angles are summarized in Table VI, and the molecular structure is shown in Figure 2.

The Pt–N bond distances of 1.936(10) and 2.002(15) Å are similar to those in the Pd(II) analogue **12′** [1.96(2) and 2.02(1) Å];[17] the same occurs between the Pt–C bond distances [1.924(17) and 1.944(13) Å] and the corresponding distances in the Pd(II) analogue **12′** [1.94(3) and 1.94(2) Å]. The chelation angles about Pt[N101–Pt1–C108

Table VI. Selected Bond Distances and Angles for 10

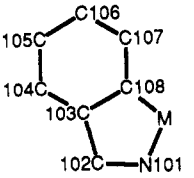
	Distances (Å)		
Pt1–N101	1.936(10)	Pt2–N201	2.002(15)
Pt1–C108	1.924(17)	Pt2–C208	1.944(13)
Pt1–O109	1.989(9)	Pt2–O209	2.016(11)
Pt1–O211	2.137(11)	Pt2–O111	2.143(10)
N101–C102	1.322(23)	N201–C202	1.299(18)
C102–C103	1.459(19)	C202–C203	1.426(20)
C102–C121	1.509(19)	C202–C221	1.524(27)
C103–C104	1.460(25)	C203–C204	1.412(22)
C104–C105	1.312(26)	C204–C205	1.345(28)
C105–C106	1.390(27)	C205–C206	1.428(32)
C106–C107	1.350(25)	C206–C207	1.365(20)
C107–C108	1.423(20)	C207–C208	1.398(21)
C103–C108	1.373(21)	C203–C208	1.419(23)
O109–C110	1.208(19)	O209–C210	1.339(21)
C110–O111	1.323(20)	C210–O211	1.221(20)
C110–C112	1.493(21)	C210–C212	1.432(27)
C121–O122	1.215(17)	C221–O222	1.147(26)
C121–C123	1.493(21)	C221–C223	1.588(22)
Pt1–Pt2	2.925(1)		
	Angles (deg)		
O109–Pt1–O211	86.1(4)	O209–Pt2–O111	87.2(4)
C108–Pt1–O109	96.4(5)	C208–Pt2–O209	93.6(6)
N101–Pt1–O211	96.1(4)	N201–Pt2–O111	97.1(4)
N101–Pt1–C108	81.3(5)	N201–Pt2–C208	82.0(6)
Pt1–N101–C102	117.4(9)	Pt2–N201–C202	114.7(10)
N101–C102–C103	112.6(13)	N201–C202–C203	116.1(14)
C102–C103–C108	113.3(15)	C202–C203–C208	114.5(12)
Pt1–C108–C103	115.1(11)	Pt2–C208–C203	112.7(11)

and N201–Pt2–C208] are less than the expected 90° for a square-planar arrangement [81.2(6) and 82.0(6)°]. The dihedral angles between planes N–Pt–C and O–Pt–O for Pt1 and Pt2 are 5.4 and 3.2°, respectively. The torsion angles N101–C102–C121–O122 and N201–C202–C221–O222 exhibit values of −74.6 and 97.0°, respectively. The Pt–Pt distance of 2.925(1) Å is slightly shorter (~0.1 Å) than those in related structures[34] and far longer than those in complexes containing a Pt–Pt bond (2.495–2.557 Å).[35]

Conclusion

The $\Delta\delta$ values, observed for C9 in all cyclometalated complexes studied in this work, unequivocally suggest a strong π-back-bonding effect of the metal on the aromatic ring. By consideration of the electron pair involved in the retrodonation, all our complexes fulfill the conditions imposed on the aromatic rings with 10 π electrons. The delocalization would be mainly reflected in the shortening of the N→Pd bond (Table VII). The N–Pd distances for different arylimine complexes found in the literature are equal to or shorter than 2.04 Å, in cyclometalated rings presumably aromatics.[36] These values are in accordance with the data obtained in our complexes.[17] On the contrary, the N–Pd distance values are longer than 2.13 Å in complexes where delocalization is not possible.[37] In cyclometalated complexes with phosphine *trans* to the C=N bond, we observed a lengthening in the N–Pd bond. This bond distance is again greater than the distance observed in complexes where delocalization is not possible.[38] The fact that the N–Pd bond distance is smaller suggests that this kind of cyclometalated ring shows some aromatic character. Therefore, we can conclude that stability associated with the aromaticity of the cyclometalated rings in the *endo* adducts obtained in the orthometalation of the arylimines could be the main factor determining their preferred formation.

Table VII. Structural Data for Cyclometalated Complexes Derived of Benzoylbenzylideneamines[a]



	7	10	2[b]	5[c]	12[d]	12'[d]
C102–N101	1.278(7)	1.322(23)	1.268(2)	1.295(6)	1.33(3)	1.30(1)
C202–N201		1.299(18)			1.35(2)	1.29(1)
C102–C103	1.456(8)	1.459(19)	1.487(2)	1.448(8)	1.44(3)	1.46(1)
C202–C203		1.426(20)			1.45(3)	1.45(1)
C103–C108	1.412(9)	1.373(21)	1.386(2)	1.400(7)	1.46(4)	1.40(1)
C203–C208		1.419(23)			1.47(3)	1.41(2)

[a] We have collected some values of the distances C108–C103, C103–C102, and C102–N101 for different complexes. These distances in **2** are respectively slightly larger, shorter, and newly larger in the complexes. This behavior is in accordance with the suggested aromatization. Nevertheless, the magnitude of these differences is too low to be accepted without reserves. [b] Fonseca, I.; Martínez-Carrera, S.; García-Blanco, S. *Acta Crystallogr.* **1982**, *B38*, 2735. [c] Unpublished data. [d] See ref 17.

Experimental Section

Infrared spectra were recorded on both Perkin-Elmer 283 (4000–600 cm^{-1}) and Perkin-Elmer 580-B (600–200 cm^{-1}) spectrophotometers. The samples were ground with KBr at a concentration of *ca.* 2% by weight and then pressed into pellets. For the region 600–200 cm^{-1}, the samples were prepared as Nujol mulls on CsI windows. NMR spectra were recorded with a $CDCl_3$ solution by using a Bruker WP-200-SY. Elemental analysis was performed on a Perkin-Elmer 240B analyzer. All the complexes gave satisfactory elemental analyses.

All solvents were purified prior to use by the standard methods.[39] Palladium(II) acetate and chloride were purchased from Strem and Johnson-Matthey, respectively. Ligand syntheses have been carried out using the published methods.[14]

Synthesis of [PdL(μ-OAc)]$_2$ (L = BNA (3), L = PEA (4)). A mixture of equimolar amounts of $Pd(OAc)_2$ with the corresponding ligands in AcOH was heated (ca. 50 °C), under N_2 for 2 h. The solvent was removed *in vacuo* and the residue extracted with CH_2Cl_2. The chromatography (SiO_2) eluting with CH_2Cl_2–EtOH (1%) gave the desired complexes, **3** (60%) and **4** (complex mixture), respectively.

Anal. Calcd for **3**: C, 59.56; H, 4.10; N, 3.02. Found: C, 59.58; H, 4.08; N, 2.98. IR: ν_{max} 1672, 1588, 1581, 1419, 604, 450 cm^{-1}.

^{1}H NMR for **4**: δ (ppm) 7.80–7.60 (m), 5.45–4.80 (m), 2.20–1.90 (m), 1.75–1.45 (m). IR: ν_{max} 1672, 1591, 1578, 1420, 614, 445 cm^{-1}.

Synthesis of [PdL(μ-Cl)]$_2$ (L = BNA (5), L = PEA (6)). Method A. To a solution of the acetato-bridged dimer in acetone was added an equimolar amount of NaCl. The solid obtained was filtered out and dried *in vacuo*, yielding **5** (87%) and **6** (42%; a unique complex was obtained), respectively.

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Table VIII. Crystal Analysis Parameters of 7

Crystal Data	
formula	$C_{24}H_{24}NO_2ClSPd$
symmetry	orthorhombic, *Pbcn*
unit cell dimens	17.975(3), 16.215(3), 15.973(3)
a, *b*, *c* (Å)	
V (Å^3), Z, D_c (g cm^{-3})	4656(3), 8, 1.519
M, $F(000)$, μ (cm^{-1})	532.38, 2160.0, 10.04
packing	
Experimental Data	
no. of reflns	
measd	3808
obsd	2439
std reflns	3 reflns every 120 min, no variation
Solution and Refinement	
solution	direct methods: MULTAN84, DIRDIF84
refinement	lesat-squares on F_o
H atoms	geometric calculations
R, R_w	0.038, 0.049

Method B. A mixture of equimolar amounts of $PdCl_2$ with the corresponding ligands in MeOH was stirred for 2 days at 25 °C. The solid obtained was filtered out and dried *in vacuo*, yielding **5** (46%) and **6** (33%), respectively.

Anal. Calcd for **5**: C, 57.29; H, 3.64; N, 3.18. Found: C, 57.31; H, 3.61; N, 3.15. IR: ν_{max} 1672, 1595, 603, 444, 315, 294 cm^{-1}.

Anal. Calcd for **6**: C, 58.17; H, 3.97; N, 3.08. Found: C, 58.12; H, 3.95; N, 3.02. IR: ν_{max} 1676, 1595, 613, 444, 307, 240 cm^{-1}.

Synthesis of [PtL(μ-Cl)]$_2$ (L = BNA (8), L = PEA (9)). To a solution of bis(μ-chloro)bis(η^3-2-methylallyl)platinum in $CHCl_3$, was added 2 equiv of the imine. This mixture was refluxed until a precipitate was formed. The precipitate was filtered out, washed with $CHCl_3$ and ether, and dried *in vacuo*, yielding **8** (84%) and **9** (69%), respectively.

Anal. Calcd for **8**: C, 47.68; H, 3.03; N, 2.65. Found: C, 47.67; H, 2.97; N, 2.63. IR: ν_{max} 1671, 1592, 606, 448, 329, 317 cm^{-1}.

Anal. Calcd for **9**: C, 48.66; H, 3.31; N, 2.50. Found: C, 48.64; H, 3.31; N, 2.50. IR: ν_{max} 1668, 1595, 614, 453, 334, 306 cm^{-1}.

Synthesis of [PtL(μ-OAc)]$_2$ (L = BNA (10), L = PEA (11)). To a suspension of $[PtLCl]_2$ in $CHCl_3$ was added an equimolar amount of AgOAc. After 10 min the whitish solution changed to red. Afterward the solution was filtered and concentrated. When MeOH was added, the deep red solid obtained was recrystallized in $CHCl_3$/MeOH, yielding **10** (80%) and **11** (76%).

Anal. Calcd for **10**: C, 49.99; H, 3.44; N, 2.53. Found: C, 49.97; H, 3.43; N, 2.49. IR: ν_{max} 1671, 1603, 1586, 1422, 610, 442 cm^{-1}.

^{1}H NMR for **11**: δ (ppm) 7.70–7.45 (m), 5.65 (m), 5.20 (m), 2.38–2.20 (m), 1.90–1.62 (m). IR: ν_{max} 1670, 1605, 1587, 1420, 615, 454 cm^{-1}.

Structure Determination and Refinement of [Pd(PEA)(DMSO)Cl] (7). A prismatic crystal (0.1 × 0.1 × 0.2 mm) was selected and mounted on a Philips PW-1100 diffractometer. Unit cell parameters were determined from automatic centering of 25 reflections ($6 \le \theta \le 12°$) and refined by the least-squares method. The data and the details of the data collection and structure analyses are summarized in Table VIII. Intensities were collected with graphite monochromatized Mo Kα radiation, using the $\omega/2\theta$ scan technique. A total of 3808 reflections were measured in the range $2 \le \theta \le 25°$, and 2439 reflections were assumed as observed by applying the condition $I \ge 2.5\sigma(I)$. Three reflections were measured every 2-h as orientation and intensity control, and no significant intensity decay was observed. Lorentz–polarization, but no absorption, corrections were made.

The structure was solved by direct methods using the MULTAN84 system of computer programs[39] and the DIRDIF84 program[40] and refined by the full-matrix least-squares method, with the SHELX76 computer program.[41] The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = [\sigma^2(F_o) + 0.155|F_o|^2]^{-1}$; f, f', and f'' were taken from ref 42. The positions of 18 H atoms were obtained from difference synthesis, while two H atoms were computed and refined using a riding model; the final R factor was 0.038 (R_w = 0.049) for all observed reflections. The number of refined parameters was 336. The maximum shift/esd = 0.1; maximum and minimum peaks in final difference synthesis were + 0.4 and −0.4 e Å^{-3}, respectively.

Table IX. Crystal Analysis Parameters of 10

Crystal Data	
formula	$C_{46}H_{38}N_2O_6Pt_2 \cdot CHCl_3$
symmetry	Triclinic, *P1*
unit cell dimens	11.371(2), 12.074(2), 16.547(3)
a, *b*, *c* (Å)	
α, β, γ (deg)	79.35(2), 89.50(3), 77.94(2)
V (Å^3), Z, D_c (g cm^{-3})	2182(1), 2, 1.863
M, $F(000)$, μ (cm^{-1})	1224.38, 1180.0, 69.7
packing	
Experimental Data	
no. of reflns	
measd	7386
osbd	4210
std reflns	3 reflns every 120 min, no variation
Solution and Refinement	
solution	Patterson
refinement	least-squares on F_o
H atoms	geometric calculations
R, R_w	0.042, 0.048

Structure Determination and Refinement of [Pt(C_6H_4-(C_6H_5C=O) C=N—$CH_2C_6H_5$)(μ-OAc)]$_2$ (10). Recrystallization by slow evaporation from a $CHCl_3$/MeOH solution produced deep red crystals. A prismatic crystal (0.1 × 0.1 × 0.2 mm) was selected and mounted on an Enraf-Nonius CAD4 diffractometer. Unit cell parameters were determined from automatic centering of 25 reflections ($16 \le \theta \le 21°$) and refined by the least-squares method. The data and the details of the data collection and structure analyses are summarized in Table IX. Intensities were collected with graphite monochromatized Mo Kα radiation, using the $\omega/2\theta$ scan technique. A total of 7386 reflections were measured in the range $2 \le \theta \le 30°$, and 4210 reflections were assumed as observed by applying the condition $I \ge 2.5\sigma(I)$. Three reflections were measured every 2 h as orientation and intensity control, and no significant intensity decay was observed. Lorentz–polarization and absorption corrections were made.

The structure was solved by Patterson synthesis using the SHELXS computer program[41] and refined by full-matrix least-squares methods with the SHELX76 computer program.[43] The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = \sigma^2(F_o)$. f, f', and f'' were taken from ref 42. Five carbon atoms of a phenyl group were located in disordered position, and an occupancy factor of 0.5 was assigned according to the height of the Fourier synthesis. The positions of 35 H atoms were computed and refined with an overall isotropic temperature factor, using a riding model, and the remaining nondisordered atoms anisotropically. The final R factor was 0.042 (R_w = 0.048) for all observed reflections. The number of refined parameters was 541. The maximum shift/esd = 0.1; maximum and minimum peaks in final difference synthesis were +0.4 and −0.3 e Å^{-3}, respectively.

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Supplementary Material Available: Listings of anisotropic thermal parameters for non-hydrogen atoms, positional and isotropic thermal parameters for hydrogen atoms, and all bond distances and angles for **7** and **10** (12 pages). Ordering information is given on any current masthead page.

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