Reactions of carbon monoxide with cyclometallated complexes of palladium(II) and platinum(II) derived from a chiral alkylbipyridine ligand

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Abstract

The reaction with CO of the six-membered cyclometallated derivatives (L)MCl (**2**, M = Pd, **3**, M = Pt; LH = 6-(1-methylbenzyl)-2,2′-bipyridine), and that of the solvato complexes [(L)M(S)][BF$_4$], (S = acetone; **4**, M = Pd; **5**, M = Pt), have been investigated at atmospheric and high pressure (80–90 atm). At atmospheric pressure the complexes **2** and **3** do not react with CO, whereas the cationic derivatives **4** and **5** afford [(L)M(CO)]$^+$ species (**6**, M = Pd; **7**, M = Pt), containing terminal CO ligands. Under higher pressure the palladium complex **2** gives a labile seven-membered acyl derivative, **9**, which either affords a benzoquinolizinone, **11**, in the presence of ethanol or undergoes reversible decarbonylation when the CO pressure is released. The platinum complex **3** undergoes reversible coordination of a carbonyl ligand, with no insertion of CO into the platinum–carbon bond.

Introduction

In a recent work we have shown that the reaction of 6-(1-methylbenzyl)-2,2′-bipyridine (**1**) (LH) with Na$_2$[PdCl$_4$] and K$_2$[PtCl$_4$] affords either the 1/1 adducts (LH)MCl$_2$ or the cyclometallated derivatives (L)MCl (M = Pd, **2**; M = Pt, **3**) depending on the reaction conditions [1]. The complexes (L)MCl are characterized by the presence of a [5,6]-ring system arising from coordination of the metal to the two nitrogen atoms and to the *ortho* carbon atom of the phenyl ring (Scheme 1).

Since six-membered cyclometallated complexes containing nitrogen donor atoms are rather uncommon [2], the palladium(II) derivative, **2**, was characterized, among other ways by an X-ray structural study [1]. This revealed that the six-membered ring adopts a boat-like conformation which does not seem to involve significant strain, the bond distances and angles within the cyclic system being normal. These features are in keeping with other X-ray structures of six-membered palladacycles described in the literature [3–5].

There is, however, a tetrahedral distortion of the coordination geometry around the metal atom, and a non-bonded interaction between the metal and one of the hydrogen atoms of the methyl group can be envisaged since the estimated distance is close to the sum of the relevant Van der Waals radii. The observation in the ^{1}H NMR spectrum of 3 of an unusual long range coupling between the methyl protons and ^{195}Pt (^5J(Pt,H) 4.5 Hz) supports the existence of such an interaction. In spite of this, metallation at the methyl group to give a pentacyclic derivative was not observed under the conditions used. This is contrary to the so-called Cope's rule according to which the formation of five-membered rings is specially favoured with N-donor ligands [6].

The rather unexpected result can be accounted in terms of the tridentate nature of the bipyridine that leads to a bicyclic system. It is possible that the steric requirements associated with such a system favour a 5.6 rather than a 5.5 fused-ring structure: we expect to find an answer to this question from the studies of the analogous reactions of 2-(1-methylbenzyl)pyridine, that we are currently making.

Alternatively, it is possible that activation of the C(sp^2)–H bond is much easier than that of a C(sp^3)–H bond, favouring the formation of the six-membered ring overall. Noteworthy, in this connection, is a recent report that either aromatic or alkyl C–H activation can be achieved, depending on the temperature and reaction time [7].

In the present paper we report some results of a study on the carbonylation of the complexes 2 and 3 that was undertaken to give further information on the reactions of the six-membered metallacycle. A preliminary report has appeared [8].

Results and discussion

Neither of complexes 2 (M = Pd) and 3 (M = Pt) reacted when carbon monoxide was bubbled into their dichloromethane solutions for several hours at room temperature. Under these mild conditions carbonyl derivatives were, however, obtained
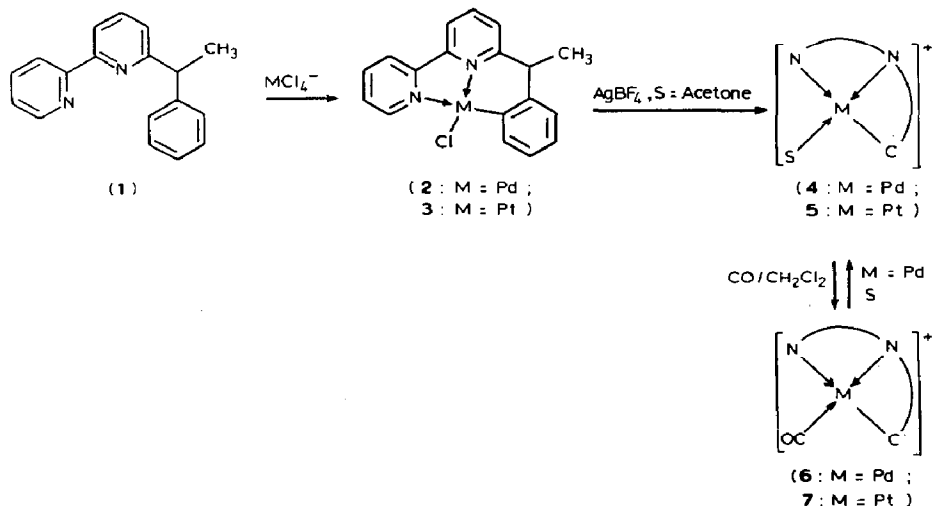
Scheme 1

from the cationic solvato species [(L)M(S)][BF$_4$] (S = acetone; M = Pd, **4**; M = Pt, **5**), which can be easily prepared by treating **2** and **3** with silver tetrafluoroborate in acetone (Scheme 1).

The acetone derivatives **4** and **5** are unusual examples of solvato complexes stable even in the solid state. Displacement of the coordinated acetone by means of carbon monoxide readily occurs in dichloromethane solution, to give the cationic terminal carbonyl complex **6** and **7**, ν(C=O) 2140 cm^{-1} and 2120 cm^{-1} for palladium and platinum, respectively. The stretching frequencies observed are in the range reported by Calderazzo and coworkers for mononuclear, neutral, or anionic palladium(II) and platinum(II) carbonyl chlorides (2167–2107 cm^{-1}) [9], as well as by others for some cyclopalladated carbonyl complexes containing aromatic oximes as ligands (2136–2108 cm^{-1}) [10].

The rather high values of the CO stretching frequencies confirm the lower tendency to π-back donation displayed by the d^8 ions of the elements of the last transition series. As this behaviour is more pronounced for palladium than for platinum, it is not surprising that the carbonyl ligand is more labile in **6** than in **7**. As a consequence, the reaction of **4** with CO can be completely reversed under very mild conditions. When **6** was suspended in acetone at room temperature, carbon monoxide was rapidly lost and the solvato complex **4** was quantitatively recovered. The platinum carbonyl derivative **7**, in contrast, is quite stable, and there is no detectable loss of CO under these conditions or upon storage in the solid state. When the reaction of **4** and **5** with carbon monoxide was carried out under more severe conditions (80–90 atm, 15–20 h), different results were obtained depending on the nature of the metal atom. Thus the platinum complex produced only the carbonyl complex **7**, whereas the palladium derivative **4** gave rise to a mixture of products from which the carbonyl **6**, containing some metallic palladium, was readily recovered by filtration in about 50% yield. Work-up of the filtrate gave moderate yields (ca. 30%) of an orange solid, not containing palladium, which was judged to be a conjugated heteroaromatic carbonyl compound (see later) on the basis of its IR spectrum. Although the formation of such a compound is indicative of an insertion of carbon monoxide into the metal–carbon bond we obtained no evidence, either in solution or in the solid state, for an acyl palladium complex.

Under these forcing reaction conditions, even the chloro complexes **2** and **3** reacted with carbon monoxide to give different products for palladium and platinum. Upon treatment with 80–90 atm of carbon monoxide in dichloromethane solution at 25–30°C for 15 h the platinum complex **3** was converted in high yield into a carbonyl derivative **8** containing a terminal metal–CO bond (ν(C=O) 2100 cm^{-1}). Compound **8** was precipitated by addition of ether, and found to be quite stable in the solid state. When its solutions were kept or when the solid was repeatedly recrystallized there was a fall in the intensity of the carbonyl band and, eventually, the starting product **3** was regenerated.

The spectroscopic and analytical data for complex **8** are in good agreement with both a cationic four-coordinated **8a** and a neutral five-coordinated **8b** derivative. After allowance for the different anion, the spectrum of the new product is seen to be quite similar to **7**, but the absence of conductivity of a freshly prepared solution of the complex in acetone favours the possibility of a neutral species, so that no clear-cut decision between the two possible structures **8a** and **8b** can be made.

In dichloromethane solution the palladium complex **2** reacted with carbon

monoxide under pressure (70–90 atm) to give a mixture of three different products, contaminated by a small amount of metal. The main product, which was isolated in 50–60% yield as orange crystals upon addition of ether, was a palladium derivative characterized by a strong absorption at 1675 cm^{-1} in the IR. This is a clear indication that insertion of carbon monoxide into the Pd–C bond of 2 had occurred, leading to the seven-membered acyl complex 9. Unfortunately, compound 9 undergoes decarbonylation very rapidly in solution, even when the solution is kept under one atmosphere pressure of carbon monoxide, and so its purification by crystallization and its further characterization by NMR were precluded. A similar facile extrusion of CO has been recently noticed in a six-membered cyclopalladated acyl complex stabilized by sulphur coordination [11].

The second product was also a palladium derivative (10): owing to its insolubility in the reaction medium it could easily be isolated as a red crystalline material contaminated by traces of metal (20–30% yield). The main feature in the IR spectrum of the crude product is a strong band at 1900 cm^{-1}. Upon treatment with most solvents the intensity of this absorption rapidly fades, and at the same time palladium is formed. Work-up gave an orange product, 11, which was identical with the third product present (5–10%) in the original reaction mixture.

The last compound 11, in the form of hydrochloride, is the exclusive product when the high pressure reaction of 2 with carbon monoxide is carried out in the presence of ethanol. Compound 11 was isolated in more than 90% yield and was fully characterized by MS and by IR, ^{1}H and ^{13}C NMR spectroscopy as 4-(2'-pyridyl)-11-methylbenzo[*b*]quinolizin-6-one. The IR spectra indicated that the same
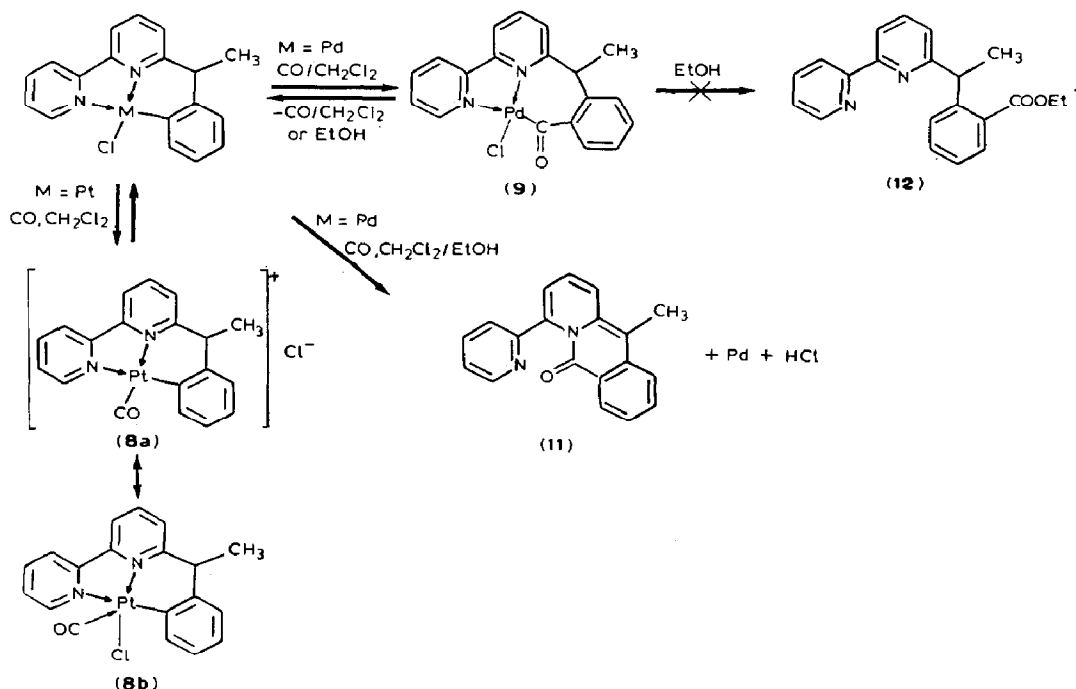
Scheme 2

compound **11**, was also obtained as the tetrafluoroborate salt in the high pressure reaction of the solvato complex **4** (see before), albeit in low yield.

Although these results, which are summarized in Scheme 2, do not even permit speculation about the exact structure of compound **10**, they suggest that this species lies along the reaction path leading to the heterocyclic product **11** from the acyl derivative **9**.

The behaviour of the palladium complex **2** towards carbon monoxide merits comment, even though on the whole it is similar to that displayed by nitrogen containing five-membered cyclopalladated derivatives [12]. Usually, these react readily with carbon monoxide, even at room temperature and atmospheric pressure [13], to give metal-free organic products. Insertion of carbon monoxide into the palladium-carbon bond, leading to an unstable six-membered acyl complex, is regarded as the key step in this process. This reasonable hypothesis is in keeping with the reaction mechanism suggested earlier by Thompson and Heck [14] in their pioneering work on the carbonylation of *ortho*-palladated aryl nitrogen complexes, but it still lacks experimental support. The few cyclopalladated acyl complexes that have been isolated up to now all contain a five-membered ring [15], and give organic products only under forcing conditions [16].

Complex **2** displays only a moderate reactivity towards carbonylation, and high pressure are required in order to bring about insertion of carbon monoxide. Despite this and the high angular strain associated with the seven-membered ring, in the absence of nucleophilic solvents the acylpalladium derivative **9** is stable enough to be isolated as a solid.

We suggest that a substantial role in the unexpected stability of **9** is played by the bipyridine system which coordinates firmly to the palladium, thus preventing the conversion of the acyl into metal-free products. It must thus be the tridentate nature of the ligand **1** that ultimately provides an extra stabilization of the intermediate metal complexes, which would be otherwise too unstable to be isolated. The low intrinsic stability of these species is confirmed by the facile loss of carbon monoxide from both the acyl derivative **9** and the terminal carbonyl complexes **6** and **8**. The preservation of the ligand framework around the metal during the decarbonylation seems to support our view.

The differing behaviour of the palladium and platinum complexes **2** and **3** reflects the lower reactivity of the platinum–carbon bond towards carbon monoxide insertion [17], and no further comment is necessary. In contrast, the reactivity towards ethanol of the cyclometallated acyl complex **9** is quite different from that of open chain acylpalladium derivatives, which give readily rise to the corresponding ethyl esters. In fact under one atmosphere of CO, complete decarbonylation of **9** occurred within few minutes, whereas under high pressure the benzoquinolizinone **11** was obtained. In no case was the expected ester **12** formed in detectable amounts. Although such behaviour of cyclopalladated acyl complexes has been previously reported [13,14], this result is quite intriguing. Since the formation of **11** cannot reasonably involve the intermediacy of **12**, it appears that the attack of the external nucleophile (ethanol) on the carbonyl group of the acyl complex **9** cannot compete with the intramolecular attack of the nitrogen responsible for the reaction path leading to the benzoquinolizinone. Since it seems more likely that ethanol promotes this process by contributing electron density to the nitrogen rather than by withdrawing it from the carbonyl group, the electron supply may be achieved at

least in two ways. First, ethanol may act as a base to assist the deprotonation of the benzylic carbon atom; alternatively, the nucleophilicity of the nitrogen may be enhanced by the addition of ethanol across the carbon–nitrogen double bond, this reaction being followed by elimination and rearrangement of the conjugated double bond system. It is our view that the latter possibility is the more likely.

Experimental

Elemental analyses were performed with a Perkin–Elmer Elemental Analyzer 240B by Mr. A. Canu (Department of Chemistry, University of Sassari) or by Pascher Mikroanalytische Laboratorium, Remagen F.D.R. Infrared spectra were recorded with Perkin–Elmer 1310 and 983 photometers. ^{1}H NMR Spectra were recorded with a Varian XL 200 or a Bruker instrument operated at 80 MHz. The mass spectrum was obtained with a VG 7070 EQ instrument under El conditions (70 eV). The ligand [6-(1-methylbenzyl)-2,2'-bipyridine] (LH) was prepared as described in ref. 18. The complexes (L)MCl (M = Pd, 2; M = Pt, 3) were prepared as previously described [1].

Preparation of [(L)M(acetone)][BF$_4$] (M = Pd, 4; M = Pt, 5)

To a solution of (L)MCl (M = Pd, 2; M = Pt, 3) (1 mmol) in acetone (20 ml) was added a solution of AgBF$_4$ (1 mmol) in the same solvent (20 ml) added. After a few minutes a white precipitate of AgCl had formed. The solution was filtered then concentrated, and diethyl ether was added to precipitate the product.

[(L)Pd(acetone)][BF$_4$] (4), pale yellow; yield 90–95%, m.p. 219–220°C. Found: C, 49.83; H, 4.22; N, 5.28. C$_{21}$H$_{21}$BF$_4$N$_2$OPd calcd.: C, 49.39; H, 4.11; N, 5.48%. Λ_M (acetone; 5×10^{-4} M): 106 ohm^{-1} cm^2 mole^{-1}. IR (nujol): ν(C=O) 1650 cm^{-1}.

[(L)Pt(acetone)][BF$_4$] (5), yellow; yield 80–85%, m.p. 220°C (dec.). Found: C, 42.62; H, 3.72; N, 4.40. C$_{21}$H$_{21}$BF$_4$N$_2$OPt calcd.: C, 42.07; H, 3.50; N, 4.67%. Λ_M (acetone, 5×10^{-4} M): 131 ohm^{-1} cm^2 mole^{-1}. IR (nujol): ν(C=O) 1625 cm^{-1}.

Reaction of [(L)M(acetone)][BF$_4$] (4 and 5) with carbon monoxide

A dichloromethane solution of 4 (or a suspension of 5) was placed in a flask equipped with a magnetic stirrer bar and connected to a vacuum line. The system was evacuated, carbon monoxide introduced, and stirring commenced. Within a few minutes a white precipitate of [(L)Pd(CO)][BF$_4$] (6) or a yellow solution of [(L)Pt(CO)][BF$_4$] (7) was formed. From the latter solution, compound 7 separated after 1 h stirring under CO. The precipitates were filtered off and washed with dichloromethane and diethyl ether.

[(L)Pd(CO)][BF$_4$] (6), yield 85–90%; m.p. 190–191°C. Found: C, 46.62; H, 3.33; N, 5.20. C$_{19}$H$_{15}$BF$_4$N$_2$OPd calcd.: C, 47.48; H, 3.12; N, 5.83%. IR (nujol): ν(C≡O) 2140 cm^{-1}.

[(L)Pt(CO)][BF$_4$] (7), yield 85–90%; m.p. 268–269°C. Found: C, 41.42; H, 3.02; N, 4.98. C$_{19}$H$_{15}$BF$_4$N$_2$OPt calcd.: C, 40.07; H, 2.63; N, 4.92%. Λ_M (acetone; 5×10^{-4} M): 110 ohm^{-1} cm^2 mole^{-1}. IR (nujol): ν(C≡O) 2120 cm^{-1}; (dichloromethane) 2100 cm^{-1}.

Reactions with carbon monoxide under high pressure. General procedure

A Pyrex bottle containing a solution of **2**, **3** or **4** was placed in a stainless steel autoclave. After removal of the air, the vessel was pressurized with CO (70–90 atm) and then rocked at room temperature for several hours. At the end of the reaction the CO was released and the mixture was worked up.

Reaction of (L)PdCl (2) with CO in dichloromethane

A dichloromethane solution of **2** (250 mg in 12.5 ml) was subjected to the procedure described above for 15 h, after which the mixture consisted of an orange solution and a dark-red precipitate. After filtration the orange solution was evaporated, and the residue extracted with diethyl ether. The residue was crystallized from CH_2Cl_2/Et_2O to give **9**, (LCO)PdCl, yield 50–60%. Found: C, 53.55; H, 3.88; N, 7.05. $C_{19}H_{15}ClN_2OPd$ calcd.: C, 53.16; H, 3.50; N, 6.53%. IR (nujol): $\nu(C=O)$ 1675 cm^{-1}.

The diethyl ether extract was evaporated to dryness and the residue recrystallized from CH_2Cl_2/n-hexane, and identified as **11**. Yield 5–10%.

The crude dark-red compound **10**, IR (nujol) $\nu(C=O)$ 1900 cm^{-1}, was extracted with $EtOH/CH_2Cl_2$. The solution was evaporated to dryness and the solid residue recrystallized from CH_2Cl_2/n-hexane to give **11**.

Reaction of (L)PdCl (2) with CO in dichloromethane/ethanol

A solution of **2** in $CH_2Cl_2/EtOH$ 4/1 (150 mg in 12.5 ml) was subjected to the general procedure described above for 24 h, after which the mixture consisted of a red solution containing palladium black. The red solution was filtered and evaporated to dryness, and the residue taken up in CH_2Cl_2. The dichloromethane solution was neutralized by stirring with K_2CO_3, then filtered, and compound **11** was precipitated by addition of n-hexane. Yield 98%; m.p. 184–185°C. Found: C, 79.54; H, 5.09; N, 9.69. $C_{19}H_{14}N_2O$ calcd.: C, 79.72; H, 4.89; N, 9.79%. IR (Nujol): $\nu(C=O)$ 1640 cm^{-1}. Mass spectrum: m/z 286. ^1H NMR (CD_2Cl_2, δ): 2.56, s, CH_3; 6.52–8.46, aromatics.

Reaction of [(L)Pd(acetone)][BF_4] (4) with CO

A solution of [(L)Pd(acetone)][BF$_4$] (**4**) in CH_2Cl_2 (80 mg in 10 ml) was treated with CO by the general procedure described above for 15 h, after which the mixture consisted of a white solid and an orange solution. The solid compound was identified as [(L)Pd(CO)][BF$_4$] (**6**) yield 60%. The orange solution was concentrated and diethyl ether was added to precipitate an orange solid, which recrystallized from CH_2Cl_2/Et_2O. M.p. 164–165°C. Found: C, 55.69; H, 4.06; N, 6.73. $C_{19}H_{14}N_2O \cdot HBF_4 \cdot 0.5\ CH_2Cl_2$: C, 56.20; H, 3.84; N, 6.72%. IR (nujol): $\nu(C=O)$ 1640 cm^{-1}.

Reaction of (L)PtCl (3) with CO in dichloromethane

A solution of (L)PtCl (**3**) in CH_2Cl_2 (100 mg in 20 ml) was treated in the usual way for 15 h. The green solution obtained was filtered to remove a small amount of platinum then concentrated. Addition of n-hexane gave compound **8** as a green yellow precipitate. Yield 70–80%; m.p. 275°C (dec.). Found: C, 44.01; H, 3.49; N, 5.18. $C_{19}H_{15}ClN_2OPt$ calcd.: C, 44.05; H, 3.09; N, 5.41%. IR (nujol); CH_2Cl_2) $\nu(C=O)$ 2100 cm^{-1}. Λ_M (acetone; 5×10^{-4} M): 3.3 ohm^{-1} cm^2 mole^{-1}.

Acknowledgements

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