Metal exchange in organomercury complexes; a facile route to cyclometallated transition metal complexes

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(Received April 27th, 1987)

Abstract

Cyclometallated derivatives of 2-phenylpyridine (HL) are readily obtained by transmetallation reactions of 2-(2'-pyridyl)phenylmercury(II) chloride, [Hg(L)Cl], with labile transition metal compounds. The products of these reactions are cyclometallated, containing metal–carbon bonds. The yields are high, and comparable with or better than those obtained from direct reactions with 2-phenylpyridine. The products are easily isolated, and are unequivocally metallated. The metal exchange reaction may be used to prepare cyclometallated complexes which are not available by direct reaction with 2-phenylpyridine. The use of the mercury(II) complex enables the use of kinetically inert chloro complexes in the transmetallation.

Introduction

The chemistry of transition metal complexes incorporating ligands such as 2,2'-bipyridine (bipy) or 2,2':6',2"-terpyridine (terpy) has recently undergone a revival [1,2]. One of the reasons for this is associated with the utilisation of such compounds as primary photocatalysts for solar energy photoconversion [3]. Where such studies have been performed, it is found that the precise nature of the ligands attached to the metal centre have profound effects upon the photochemical and redox properties [4]. The discovery that the 'anomalous', but photoactive "{Ir(bipy)$_3$}$^{n+}$ complexes incorporated a cyclometallated 2,2'-bipyridine ligand [5], led us to investigate methods for the designed synthesis of such complexes. The photophysical properties of the cyclometallated derivatives are different from those of the 'normal' complexes [6]. The replacement of the nitrogen donor atom by a carbon affects the metal-centred electron density, and affords higher energy ligand field excited states [7].

We were interested in the development of general routes for the synthesis of cyclometallated complexes. Although numerous metallated derivatives of 2-phenyl-

pyridine and its congeners are known [8], their synthesis is frequently serendipitous. However, although the insertion of a transition metal into an aromatic C–H bond may require forcing conditions, mercuration is a relatively facile process [9]. We report herein metal-exchange reactions of the readily-prepared compound [Hg(L)Cl] with labile transition metal species to yield cyclometallated complexes.

Results and discussion

Mercury(II) acetate reacts smoothly with 2-phenylpyridine in ethanol to yield [Hg(L)(OAc)], which is converted into [Hg(L)Cl] upon metathesis with lithium chloride [10]. A considerable amount of a bis-mercurated derivative, 1,3-bis(chloromercurio)-6-(2-pyridyl)benzene, was also obtained in this preparation as a very insoluble white compound (Scheme 1). The factors favouring the facile electrophilic attack of mercury(II) salts upon aromatic compounds have been discussed elsewhere [11].

The compound [Hg(L)Cl] has not been structurally characterised, but is thought to be a three coordinate cyclometallated complex (1), although binuclear, chloride-bridged structures cannot be eliminated. McWhinnie has demonstrated the use of [Hg(L)Cl] in the preparation of organotellurium compounds [10].

We have previously demonstrated the preparation of $[Ru(bipy)_2L]^+$ salts by the reaction of 2-phenylpyridine with $[Ru(bipy)_2Cl_2]$ in the presence of two equivalents of silver(I) [12]. The reaction of [Hg(L)Cl] with $[Ru(bipy)_2Cl_2]$ did not yield this complex, but gave dark-coloured, uncharacterised products. However, in the pres-
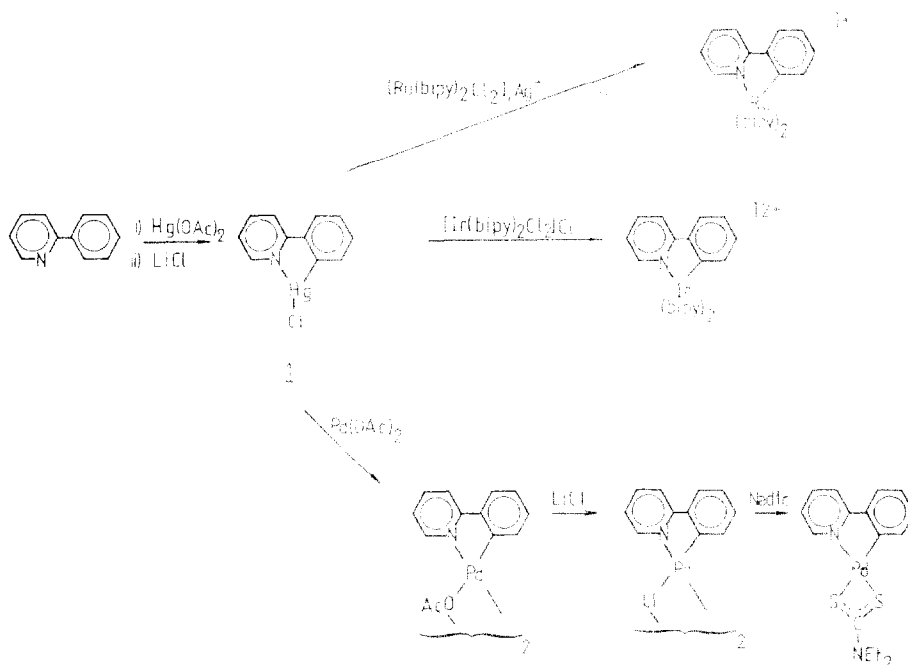
Scheme 1

ence of three equivalents of silver(I) tetrafluoroborate, reaction proceeded smoothly, to give a purple-red solution, from which [Ru(bipy)$_2$L][PF$_6$] may be isolated as a deep red solid in 45% yield after the addition of ammonium hexafluorophosphate. The complex is readily purified by affinity chromatography over Sephadex LH-20 in acetone. The infra-red and ^{1}H NMR spectra of the complex were identical to those previously reported.

The reaction of 2-phenylpyridine with palladium(II) acetate or palladium(II) chloride is reported to yield a mixture of cyclometallated and unmetallated complexes, which is difficult to separate [13]. We considered that the mercury-palladium exchange reaction might provide an unequivocal preparation for the cyclometallated complex. The reaction of [Hg(L)Cl] with palladium(II) acetate in ethanol/dichloromethane gave a deep yellow solution, from which the complex [LPd(μ-OAc)$_2$PdL] was obtained in quantitative yield. The complex exhibits absorptions in its infrared spectrum at 1571 and 1416 cm^{-1}, which may be assigned to the asymmetric and symmetric stretching modes, respectively [14]. The difference between these two modes is a function of the chemical environment of the acetate group; typically, monodentate acetate exhibits a difference of 250 cm^{-1}, chelating acetate of 50 cm^{-1} and bridging acetate of 150 cm^{-1}. The difference observed for our compound of 155 cm^{-1} characterises it as the μ-acetato complex.

The ^{1}H NMR spectrum of a CDCl$_3$ solution of the complex exhibits a single resonance at δ 2.22 ppm, which may be assigned to the methyl groups of the bridging acetate. The aromatic region of the spectrum of a CDCl$_3$ solution of the complex is shown in Fig. 1. The fluxional processes occurring in such acetato-bridged complexes have been discussed elsewhere, and are probably responsible for the broadening of these signals. A solution of the complex in CD$_3$SOCD$_3$ exhibits a rather different spectrum, in which all of the aromatic signals have experienced a downfield shift. In particular, the spectrum exhibits two resonances for the acetate methyl groups, which may be assigned to free and coordinated acetate, and we believe the solution species to be [PdL(dmso)(OAc)].

The reaction of [LPd(μ-OAc)$_2$PdL] with lithium chloride results in quantitative conversion into the very insoluble yellow complex, [LPd(μ-Cl)$_2$PdL]. This chloro-bridged complex is converted into the neutral species [LPd(S$_2$CNEt$_2$)] upon treating with sodium dithiocarbamate in aqueous methanol. The ^{1}H NMR spectrum of the complex exhibits two non-equivalent ethyl groups, as expected for a square-planar palladium(II) complex in which the lone pair of the dithiocarbamate nitrogen is delocalised, and rotation about the C–N bond is restricted [15]. It is noteworthy that the methyl groups are more sensitive to the environment than the methylene groups; the former appear as two triplets centred at δ 1.38 and 1.31 ppm, whereas the latter are coincident, and appear as a single quartet at δ 3.86 ppm. The aromatic region of the ^{1}H NMR spectrum of the complex is shown in Fig. 1.

Attempts to prepare [Ir(bipy)$_2$L]$^+$ salts by the direct reaction of [Ir(bipy)$_2$Cl$_2$]Cl or [Ir(bipy)$_2$Cl$_2$][PF$_6$] with 2-phenylpyridine is a variety of conditions were unsuccessful; in all cases, the iridium species were recovered unchanged. The chloride ligands in [Ir(bipy)$_2$]$^+$ are known to be substitution inert [16], and it is extremely difficult to prepare [Ir(bipy)$_3$]$^{3+}$ complexes from this source. The addition of silver(I) salts had no effect upon the reaction with 2-phenylpyridine, and [Ir(bipy)$_2$Cl$_2$]$^+$ salts were recovered unchanged, even after prolonged reaction times. However, [Ir(bipy)$_2$Cl$_2$]Cl reacted with ethanolic solutions of [Hg(L)Cl] to yield
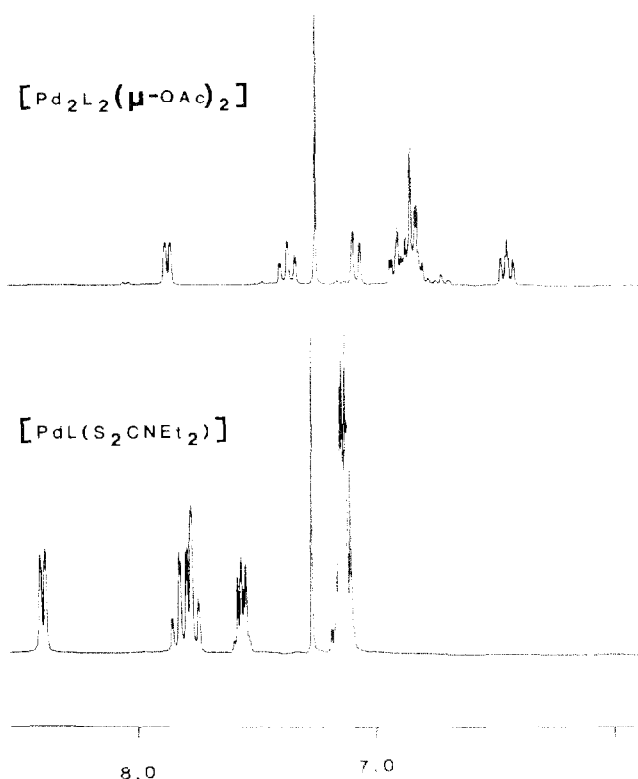
Fig. 1. (a) The aromatic region of the ¹H NMR spectrum of [LPd(μ-OAc)₂PdL] (CDCl₃, 250 MHz); (b) the aromatic region of the ¹H NMR spectrum of [LPd(S₂CNEt₂)] (CDCl₃, 250 MHz).

deep-orange solutions, in the absence of silver(I) salts. The salt [Ir(bipy)₂L][PF₆]₂ was obtained in 68% yield as a bright yellow solid upon the addition of ammonium hexafluorophosphate.

The ¹H NMR spectrum of the complex differs from that of the analogous ruthenium(II) complex, in that the C/D and E/F rings of the 2,2'-bipyridine ligands now appear to be chemically and magnetically equivalent. The spectrum exhibits signals due to 16 unique protons, eight of intensity two, assigned to the 2,2'-bipyridine ligands, and eight with intensity one assigned to the cyclometallated 2-phenylpyridine. The protons attached to the metallated phenyl ring are clearly seen at δ 8.57(d), 7.97(t), 7.64(m) and 7.41(d) ppm (Fig. 2).

It is known that mercury(II) salts provide a metal-assisted pathway for the labilisation of halide ions in kinetically inert complexes [17], and we believe that the [Hg(L)Cl] plays a dual role in this synthesis, both as a source of the ligand, and in labilising the chloride groups.

In conclusion, we have shown that the cyclometallated complex [Hg(L)Cl] undergoes facile transmetallation reactions with transition metal compounds. The products of these reactions are cyclometallated, and the yields are high and comparable, or superior to, those obtained from direct reactions with 2-phenylpyridine. The products are easily isolated, and are unequivocally metallated. The metal
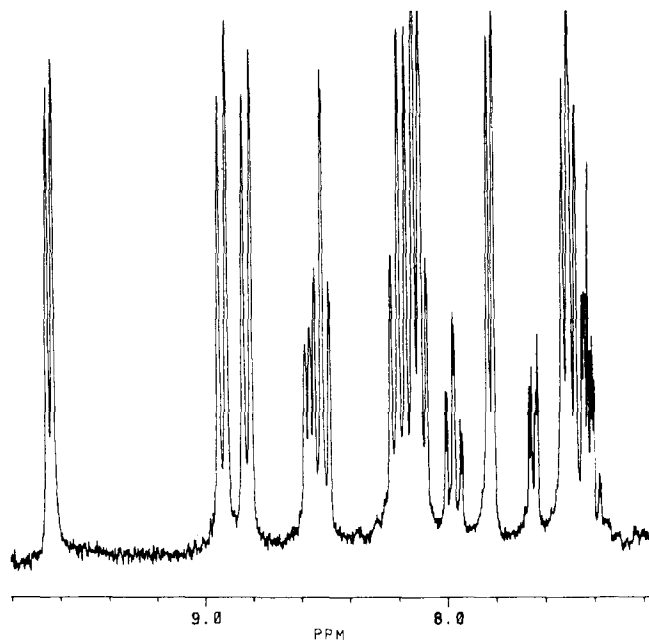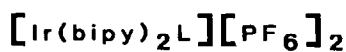
$$[Ir(bipy)_2L][PF_6]_2$$

Fig. 2. The aromatic region of the ^{1}H NMR spectrum of [Ir(bipy)$_2$L][PF$_6$]$_2$ (CD$_3$SOCD$_3$, 250 MHz).

exchange reaction may be used to prepare cyclometallated complexes which are not available by direct reaction with 2-phenylpyridine. The use of the mercury(II) complex enables the use of kinetically inert chloro complexes in the transmetallation.

Experimental

2-Phenylpyridine (Aldrich), silver(I) tetrafluoroborate (Aldrich), palladium(II) acetate (Johnson–Matthey), 'ruthenium trichloride trihydrate' (Johnson–Matthey), and iridium(III) chloride (Johnson–Matthey) were used as received. Sephadex LH-20 (Sigma) was pre-equilibrated with the elution solvent prior to use. The complexes [Hg(L)Cl] [10], [Ru(bipy)$_2$Cl$_2$] [18] and [Ir(bipy)$_2$Cl$_2$]Cl [19] were prepared by the literature methods. ^{1}H NMR spectra were recorded using Bruker WM 250 or AM 400 spectrometers in CD$_3$SOCD$_3$, CD$_3$COCD$_3$, or CDCl$_3$ solution. Infrared spectra were recorded using Perkin–Elmer 983 or 1700 spectrophotometers. Reactions were performed under an atmosphere of dry dinitrogen where appropriate.

2-(2'-Pyridyl)phenylmercury(II) chloride, [Hg(L)Cl]

A mixture of 2-phenylpyridine (3.67 g, 0.023 mol) and mercury(II) acetate (7.50 g, 0.023 mol) in absolute ethanol (50 cm^3) was heated under reflux for 24 h, and a

solution of lithium chloride (2.1 g) in methanol (50 cm^3) was then added. The mixture was heated for 15 min, then added to distilled water (150 cm^3). The white precipitate was filtered off and washed with water and ice-cold methanol. The solid was extracted with hot methanol, to leave the bis-mercurated product as a solid residue (4.55 g, 63%). Cooling of the methanolic extract caused separation of an off-white crystalline solid, which was filtered off, washed with ice-cold methanol, and dried, to yield [Hg(L)Cl] (2.04 g, 23%). (Found: C, 34.0; H, 2.3; N, 3.5. C$_{11}$H$_8$NHgCl calcd.: C, 33.8; H, 2.05; N, 3.6%.)

Bis(2,2'-bipyridine){2-(2'-pyridyl(phenyl}ruthenium(II) hexafluorophosphate, [Ru-(bipy)$_2$L][PF$_6$]

A suspension of [Hg(L)Cl] (20 mg, 0.05 mmol) and [Ru(bipy)$_2$Cl$_2$] (24 mg, 0.05 mmol) in ethanol (30 cm^3) was heated under reflux with silver(I) tetrafluoroborate (29 mg, 0.15 mmol) for 4 h and then filtered through Celite. The deep red filtrate was reduced to about 15 cm^3 volume in vacuo and treated with methanolic [NH$_4$][PF$_6$]. The purple precipitate obtained was filtered off and dissolved in acetone, and the solution was filtered through Celite then evaporated to dryness to yield the title complex (16 mg, 45%). Chromatography of an acetone solution over Sephadex LH-20 gave one major purple band (98%), and two weaker bands, which were not collected. (Found: C, 52.0; H, 3.3; N, 9.7. C$_{31}$H$_{24}$N$_5$F$_6$PRu calcd.: C, 52.2; H, 3.4; N, 9.8%.) Infrared: 1599, 1572, 1470, 1459, 1442, 1417, 758, 739, 730 cm^{-1}.)

2-(2'-Pyridyl(phenylpalladium(II) acetate, [LPd(μ-OAc)$_2$PdL]

A suspension of [Hg(L)Cl] (0.195 g, 0.5 mmol) in ethanol (20 cm^3) was added to a solution of palladium(II) acetate (0.113 g, 0.5 mmol) in CH$_2$Cl$_2$ (8 cm^3), and the mixture heated under reflux for 4 h. The deep yellow solution was then filtered through Celite, and the filtrate concentrated in vacuo until a solid began to separate. The solid was filtered off and dried, to yield [LPd(μ-OAc)$_2$PdL] · $\frac{1}{2}$H$_2$O as a yellow solid (0.130 g, 100%). (Found: C, 48.1; H, 3.4; N, 4.35. C$_{26}$H$_{23}$N$_2$Pd$_2$O$_{4.5}$ calcd.: C, 48.2; H, 3.55; N, 4.3%.)

2-(2'-Pyridyl)phenylpalladium(II) chloride, [LPd(μ-Cl)$_2$PdL]

A suspension of [LPd(μ-OAc)$_2$PdL] (0.080 g, 0.125 mmol) in methanol (10 cm^3) was stirred with lithium chloride (0.5 g) for 1 h after which the pale yellow solid was filtered off and dried, to yield the [Pd$_2$L$_2$Cl$_2$] · 2H$_2$O · 2LiCl (0.074 g, 84%). (Found: C, 37.4; H, 2.7; N, 4.0. C$_{22}$H$_{20}$N$_2$Pd$_2$Cl$_4$Li$_2$O$_2$ calcd.: C, 37.5; H, 2.8; N, 4.0%.)

2-(2'-pyridyl)phenyl(N,N-diethyldithiocarbamato)palladium(II), [PdL(S$_2$CNEt$_2$)]

A mixture of sodium diethyldithiocarbamate (0.045 g, 0.2 mmol) and [LPd(μ-Cl)$_2$PdL] (0.070 g, 0.1 mmol) in aqueous methanol (1/1, 15 cm^3) was heated under reflux for 12 h. The yellow suspension was filtered hot, and the solid dried to yield [PdL(S$_2$CNEt$_2$)] (0.060 g, 72%). (Found: C, 45.6; H, 4.7; N, 6.9. C$_{16}$H$_{19}$N$_2$PdS$_2$O$_{0.5}$ calcd.: C, 46.0; N, 4.55; H, 6.7%.)

Bis(2,2'-bipyridine)(2-(2'-pyridyl)phenyl)iridium(III) hexafluorophosphate, [Ir(bipy)$_2$-L][PF$_6$]$_2$

A solution of [Ir(bipy)$_2$Cl$_2$]Cl (30 mg, 0.05 mmol) and [Hg(L)Cl] (20 mg, 0.05 mmol) in ethanol (25 cm^3) was heated under reflux for 6 h, and the yellow solution

was then filtered through Celite, concentrated in vacuo, and treated with $[NH_4][PF_6]$ to give a bright yellow precipitate of the $[Ir(bipy)_2L][PF_6]_2 \cdot 2.5H_2O \cdot HPF_6$ (32 mg, 68%). (Found: C, 32.6; H, 2.7; N, 6.6. $C_{31}H_{30}N_5IrP_3F_{18}O_{2.5}$ calcd.: C, 32.6; H, 2.6; N, 6.2%.)

Acknowledgements

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