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TRANSITION METAL—CARBON BONDS

XL*. PALLADIUM(II) COMPLEXES OF [(DIMETHYLAMINO)METHYL]-FERROCENE

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Summary

$C_5H_5FeC_5H_4CH_2NMe_2$ reacts with sodium chloropalladate(II) in the presence of sodium acetate to give the internally metallated binuclear species $[\overline{Pd_2X_2\{C_5H_5FeC_5H_3CH_2N}Me_2\}_2]$ (X = Cl). The corresponding iodide was prepared as were mononuclear species $[\overline{Pd(acac)\{C_5H_5FeC_5H_3CH_2N}Me_2\}]$ and $[\overline{Pd\{C_5H_5FeC_5H_3CH_2N}Me_2\}L]$ L = PMe_2Ph, $AsMe_2Ph$, $P(OMe)_3$ or PPh_3. ^1H NMR data are given.

Introduction

One of the first examples of an internal metallation reaction by a transition metal was the work of Cope and Friedrich [2] who showed that *N,N*-dimethylbenzylamine was readily palladated when treated with lithium chloropalladate, to give $[\overline{Pd_2Cl_2(C_6H_4CH_2N}Me_2)_2]$. In this reaction, as with the palladation of azobenzene, it was considered that the metal acts as an electrophile. One might therefore expect that [(dimethylamino)methyl]ferrocene would undergo palladation very readily since it is well known that a ring in ferrocene is much more susceptible to electrophilic attack than a benzene ring [3]. However, Moynahan et al. [4] were unsuccessful in their attempts to metallate dimethylaminomethylferrocene (L); the complex $[PdCl_2L_2]$, containing the unmetallated ligand, was obtained. These authors treated potassium chloropalladite with dimethylaminoferrocene (L) in dioxan containing a little water at room temperature: a procedure which immediately gave $[PdCl_2L_2]$, as a yellow precipitate.

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* For part XXXIX see ref. 1.

TABLE 1

ANALYTICAL, MOLECULAR WEIGHT, AND MELTING POINT DATA FOR SOME PALLADIUM(II) INTERNALLY METALLATED COMPLEXES OF [(DIMETHYLAMINO)METHYL] FERROCENE

C—N ≡ $C_5H_5FeC_5H_3CH_2NMe_2$

Compound	Colour	Yield(%)	Analytical data[a]				Mol weight[a,b]	M.p. (°C)
			C	H	Halogen	N		
$[Pd_2Cl_2(C—N)_2]$	Orange	84	40.7(40.7)	4.5(4.2)	9.1(9.2)	3.7(3.65)	771(774)	c
$[PdCl(C—N)\{P(OMe)_3\}]$	Yellow	50	38.0(37.8)	5.3(5.0)	7.4(7.0)	2.95(2.75)	519(508)	134-142[d]
$[PdI(C—N)\{P(OMe)_3\}]$	Yellow	60	32.4(32.05)	4.45(4.2)	21.35(21.2)	2.1(2.3)	598(599)	145-148[e]
$[PdCl(C—N)(PMe_2Ph)]$	Brown	52	48.4(48.3)	5.2(5.2)	6.5(6.8)	2.5(2.7)	527(522)	175-176
$[PdCl(C—N)(AsMe_2Ph)]$	Brown	73	44.3(44.55)	4.85(4.8)	6.15(6.3)	2.7(2.5)	573(566)	178-180[e]
$[PdI(C—N)(AsMe_2Ph)]$	Red	33	38.2(38.4)	4.2(4.3)	19.25(19.3)	2.15(2.1)		65-70
$[PdCl(C—N)(PPh_3)]$	Red	80	57.1(57.6)	4.8(4.8)	5.65(5.5)	2.2(2.2)	666(646)	f
$[PdI(C—N)(PPh_3)]$	Red	77	50.5(50.5)	4.25(4.2)	17.0(17.2)		748(738)	f
$[Pd(acac)(C—N)]$	Brown	71	48.6(48.3)	5.2(5.2)		3.35(3.1)	438(448)	119-126

[a] Calculated values in parentheses. [b] Chloroform solution. [c] Decomposes without melting, 172-175°C [d] Melts with gas evolution. [e] Melts with decomposition. [f] Decomposes above 150°C.

TABLE 2

^{1}H NMR DATA FOR SOME INTERNALLY METALLATED COMPLEXES OF PALLADIUM(II) WITH [(DIMETHYLAMINO)METHYL] FERROCENE

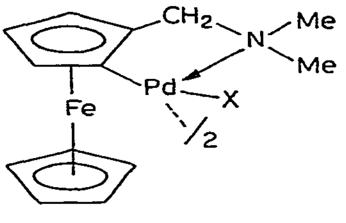
Data were recorded at 60 MHz and ca. 34°C in $CDCl_3$ solution with TMS as internal standard. δ values ± 0.02 *J* values ± 0.5 Hz d = 1/1 doublet s = singlet
C—N ≡ $C_5H_5FeC_5H_3CH_2NMe_2$

Compound	δ(N—Me)		δ(P—Me), (P—OMe) or (As—Me)	
$[Pd_2Cl_2(C—N)_2]$	305s,	2.89s		
[Pd(acac)(C—N)] [a]	308s,	2.86s		
$[PdCl(C—N)(PMe_2Ph)]$	3.15d	$^4J(PH) = 2.6$	2.00d	$^2J(PH) = 11.6$
	2.87d	$^4J(PH) = 2.5$	1.94d	$^2J(PH) = 11.5$
$[PdI(C—N)(PMe_2Ph)]$	3.28d	$^4J(PH) = 2.7$	2.16d	$^2J(PH) = 10.7$
	2.93d	$^4J(PH) = 2.7$	2.07d	$^2J(PH) = 10.6$
$[PdCl(C—N)(AsMe_2Ph)]$	3.19s,	2.93s	1.89s,	1.82s
$[PdI(C—N)(AsMe_2Ph)]$	3.42s,	3.06s	2.08s,	2.03s
$[PdCl(C—N)\{P(OMe)_3\}]$	3.05d	$^4J(PH) = 4.0$	3.90d	$^3J(PH) = 12.9$
	2.77d	$^4J(PH) = 3.2$		
$[PdI(C—N)\{P(OMe)_3\}]$	3.25d	$^4J(PH) = 4.2$	3.90d	$^3J(PH) = 13.4$
	2.83	$^4J(PH) = 3.2$		
$[PdCl(C—N)(PPh_3)]$	3.22d	$^4J(PH) = 4.2$		
	3.09d	$^4J(PH) = 3.2$		

[a] acac group: δ(C—H) = 5.45s, δ(CH_3) = 2.025, 1.98s.

Results and discussion

We find that treatment of sodium chloropalladate with dimethylaminoferrocene in methanol also produces $[PdCl_2L_2]$ containing the unmetallated ligand. However, when mole equivalents of sodium tetrachloropalladate(II) (dimethylamino)methylferrocene and sodium acetate trihydrate were stirred together in methanol for two hours a new complex was obtained. This, on the basis of microanalytical, molecular weight and spectroscopic data (Tables 1 and 2) and reactions (see below) was shown to be the desired complex $[PdX(C_5H_3CH_2NMe_2)FeC_5H_5]_2$ (I) (X = Cl) (see Fig. 1). We have previously shown that acetate



(I)

ion promotes internal metallation reactions [5,6]. In the ^{1}H NMR spectrum of I (X = Cl) the *N*-methyls are non-equivalent, as expected. In the far IR spectrum (400-200 cm^{-1}) there are three bands assigned to ν(Pd—Cl) at 318, 284 and 255 cm^{-1} and which are absent from the spectrum of the corresponding iodide (I) (X = I), prepared from the chloride by metathesis (see Experimental). $[Pd_2Cl_2(C_6H_4CH_2NMe_2)_2]$ shows two bands due to ν(Pd—Cl), at 330 and 247 cm^{-1} [7].

Presumably the band at 284 for our compound is due to a solid state effect. The complex I (X = Cl) shows reactions typical of a chlorine bridged binuclear complex of palladium e.g. when treated with thallous acetylacetonate the mononuclear acetylacetonate $[\overline{Pd(acac)\ (C_5H_3CH_2N}Me_2)FeC_5H_5]$ was produced, see Experimental and Tables for characterizing data. The acac, *N*-methyl and *N*-methylene resonances for this complex were readily assigned (Table 2) but the resonances due to the substituted ferrocene ring were broad and complex. However, double irradiation of a small shoulder on the high field side of the π-C_5H_5 singlet (δ 4.16) caused a broad resonance at δ 3.99 to change to an AB-pattern due to two adjacent protons on the substituted ferrocene ring. The chloro-bridged complex $[\overline{Pd_2Cl_2(C_5H_3CH_2N}Me_2)FeC_5H_5]_2$ (I) (X = Cl) readily underwent bridge-splitting reactions with ligands such as PMe_2Ph, $P(OMe)_3$ or PPh_3. The complexes were characterized by microanalytical and ^1H NMR data (see Tables). Unfortunately the far IR spectra are complex and we could not assign values of ν(Pd—Cl) even after comparing the IR spectra with those of the corresponding iodides. We do not know therefore whether in a bridge-split product the bridge-splitting ligand L is opposite nitrogen or carbon. The ^1H NMR spectra show that on splitting the chlorine bridges by L one product is formed and that on the NMR time scale exchange of the ligand L is slow since, for example, in the ^1H NMR spectrum of $[PdCl(C_5H_5FeC_5H_3CH_2NMe_2)\ (PMe_2Ph)]$ the resonance due to each *N*-methyl group is a doublet due to splitting by phosphorus; a similar splitting is observed for the analogous complexes (Table 2). The phosphorus methyls are non-equivalent in this complex and each forms a doublet again as would be expected. Other NMR data are given in Table 2 and are in agreement with the assigned structures.

Experimental

The general experimental and instrumental methods are similar to those reported in other papers from this laboratory. (Dimethylamino)methylferrocene was prepared by a literature method [8].

Di-μ-chlorobis-[2-{(dimethylamino)methyl}ferrocenyl]dipalladium(II)

(Dimethylamino)methyl ferrocene (4.23 g, 17.4 mmol) in methanol (5 ml) was added to a mixture of sodium tetrachloropalladite(II) (5.17 g, 17.4 mmol) and sodium acetate trihydrate (2.37 g, 17.4 mmol) in methanol (30 ml). The mixture was stirred for 2 h and the precipitate which formed was filtered off, and dried (Yield: 5.64 g, 7.27 mmol). A portion was recrystallised from methanol.

Acetylacetonato-[2-{(dimethylamino)methyl} ferrocenyl]palladium(II).

A suspension of thallous acetylacetonate (0.79 g, 2.42 mmol) and di-μ-chlorobis-[2-{(dimethylamino)methyl} ferrocenyl] dipalladium(II) (0.98 g, 1.27 mmol) in benzene (20 ml) was stirred for 12 h, and then filtered. The filtrate was evaporated under reduced pressure, giving a red oil. The product (0.77 g, 1.715 mmol) was obtained as prisms from light petroleum (b.p. 30-40°C).

Chloro-[2-{(dimethylamino)methyl} ferrocenyl](dimethylphenylphosphine)-palladium(II)

Di-μ-chlorobis-[2-{(dimethylamino)methyl}-ferrocenyl] dipalladium(II)

(1.25 g, 1.65 mmol) was suspended in benzene (15 ml), under an atmosphere of argon. Dimethylphenylphosphine (0.50 g, 3.62 mmol) was added to the suspension, and the mixture was stirred for 1 h. All the solid dissolved, giving a red solution. The solvent was removed under reduced pressure, giving a red oil. This was triturated with diethyl ether to give a yellow solid. The product (0.89 g, 1.72 mmol) was obtained as prisms from methanol.

Chloro-[2-{(dimethylamino)methyl}ferrocenyl](triphenylphosphine)palladium (II)

Triphenylphosphine (0.17 g, 0.64 mmol) and di-μ-chlorobis-[2-{(dimethylamino)methyl}ferrocenyl] dipalladium(II) (0.245 g, 0.32 mmol) were dissolved in benzene (15 ml), and stirred for 0.5 h. The solvent was removed under reduced pressure, and the product (0.33 g, 0.51 mmol) was obtained as prisms from dichloromethane-methanol.

Chloro-[2-{(dimethylamino)methyl} ferrocenyl](dimethylphenylarsine)palladium(II)

Dimethylphenylarsine (0.51 g, 2.8 mmol) was added to a suspension of di-μ-chlorobis-[2-{(dimethylamino)methyl} ferrocenyl]dipalladium(II) (1.02 g, 1.33 mmol) in benzene (15 ml), under an atmosphere of argon. The solid dissolved, and the solution was stirred for 0.5 h. Then the solvent was removed under reduced pressure, giving an orange oil. This was triturated with diethyl ether to give a yellow solid. The product (1.10 g, 1.94 mmol) was obtained as prisms from methanol.

Chloro-[2-{(dimethylamino)methyl}ferrocenyl](trimethylphosphite)palladium-(II)

Trimethyl phosphite (0.225 g, 181 mmol) was added to a suspension of di-μ-chlorobis-[2-{(dimethylamino)methyl}ferrocenyl] dipalladium(II) (0.66 g, 0.86 mmol) in benzene (15 ml). The suspension was stirred for 2 h, during which time all the solid dissolved. The solvent was removed under reduced pressure, and the product (0.44 g, 0.87 mmol) was obtained as plates from methanol.

Iodo-[2-{(dimethylamino)methyl}ferrocenyl](trimethylphosphite)palladium(II)

Chloro-[2-{(dimethylamino)methyl}ferrocenyl](trimethylphosphite)palladium(II) (0.16 g, 0.32 mmol) was suspended in acetone (10 ml) with sodium iodide (0.20 g). The suspension was heated under reflux for 10 min, and the solvent was then removed under reduced pressure. The solid was washed with water, filtered, and dried. This procedure was repeated, and the product (0.115 g, 0.192 mmol) was obtained as plates from methanol.

The following compounds were similarly prepared from the corresponding chlorides: iodo-[2-{(dimethylamino)methyl}ferrocenyl] (dimethylphenylphosphine)palladium(II); iodo-[2-{(dimethylamino)methyl} ferrocenyl] (dimethylphenylarsine)palladium(II); iodo-[2-{(dimethylamino)methyl}ferrocenyl] (triphenylphosphine)palladium(II).

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