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NOTE

FERROCENE STUDIES
III*. PLATINUM AND PALLADIUM COMPLEXES OF [(DIMETHYLAMINO)METHYL]FERROCENE

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INTRODUCTION

Cope and Friedrich[2] have shown that when a solution of *N*,*N*-dimethylbenzylamine is allowed to react with $K_2[PtCl_4]$ a binuclear complex, di-μ-chlorobis{2-[(dimethylamino)methyl]phenyl}diplatinum(II) (I) is formed containing a metal to carbon σ-bond. A similar complex was formed from the same amine and $Li_2[PdCl_4]$[2]. Azobenzene also led to a similar complex[3] and it was further shown[4] that this latter complex reacted with carbon dioxide to yield a series of 2-aryl-3-indazolinones. If similar complexes, containing a metal to carbon σ-bond, could be prepared, these might supply convenient intermediates for further synthetic sequences in the ferrocene series.

RESULTS

Reaction of [(dimethylamino)methyl]ferrocene (II) in dioxane with $K_2[PdCl_4]$ gave dichlorobis{[(dimethylamino)methyl]ferrocene}palladium(II) (III). Structure (III) was consistent with the IR and NMR spectra of the compound. Reaction of (III) with triphenylphosphine in a ligand replacement reaction gave a quantitative yield of $[(C_6H_5)_3P]_2PdCl_2$, as identified by comparison with an authentic sample.

Reaction of [(dimethylamino)methyl]ferrocene (II) as its hydrochloride salt in aqueous solution with $K_2[PdCl_4]$ gave rise to a complex differing in structure from (III). Use of $K_2[PtCl_4]$, $Na_2[Pd(CN)_4]$, and $Na_2[Pt(CN)_4]$ with (II) under these same conditions gave similar products.

Although these four new complexes differed in structure from (III) an examination of the elemental analysis, IR and NMR spectra, conductivity measurements, and reactions indicated that they were not the desired ferrocene analogues of (I).

Ligand replacement reactions of the four complexes with triphenylphosphine gave $[(C_6H_5)_3P]_2PdCl_2$ or $[(C_6H_5)_3P]_2PtCl_2$. Reaction of the complex formed

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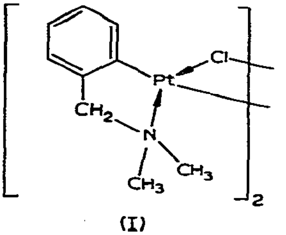
[*] For Part II see ref. 1.

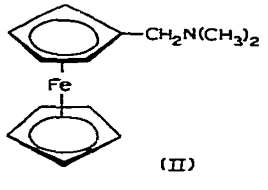
from the $Na_2[Pd(CN)_4]$ with $NaB(C_6H_5)_4$ in water gave $\{Fc[CH_2N(CH_3)_2H\}^+$-$\{BPh_4\}^-$. Reaction of the four complexes with tetraphenylarsonium chloride gave $[(C_6H_5)_4As]_2[MX_4]$. Conductivity measurements on the palladium complexes in dimethyl sulfoxide and the platinum complexes in methanol gave equivalent conductivities consistent with the structures below.

No amine hydrochloride absorption (2400–2800 cm^{-1}) was observed in the IR spectra of nujol mulls of these four compounds, although this band was present when the spectra were taken in dimethyl sulfoxide. All of the ferrocene compounds exhibited the typical 9, 10 absorption. The NMR spectra of (II) hydrochloride, (III), and these four complexes were all very similar. Further details on the IR and NMR spectra are included in the Experimental Section.

On the basis of the available information it would appear that these four complexes can best be represented by (IV) where M is platinum or palladium and X is chloro or cyano.



(I)



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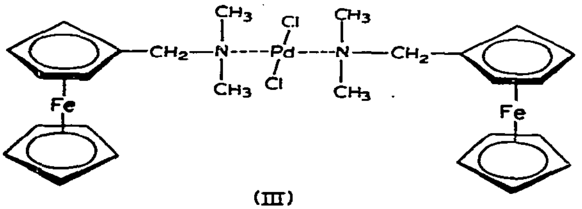
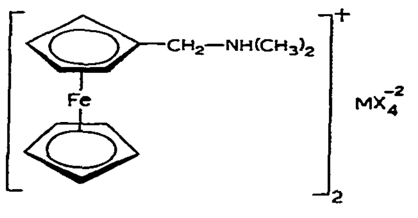


(III)



(IV)

EXPERIMENTAL

All melting points are corrected. Analyses by Spang Microanalytical Laboratory, Ann Arbor, Michigan and Galbraith Laboratories, Knoxville, Tenn. IR spectra were run as nujol mulls and NMR spectra were run in DMSO-d_6 with TMS as an external standard unless otherwise noted.

Dichlorobis{[(dimethylamino)methyl]ferrocene}palladium(II) (III)

A solution of 0. 5 g of $K_2[PdCl_4]$ in 20 ml of water was added dropwise at room temperature to a stirred solution of 0.8 g of [(dimethylamino)methyl]ferrocene (II) in 20 ml of dioxane. The yellow precipitate which formed immediately was filtered and washed successively with several portions of water and then diethyl ether. The solid, (0.83 g, 82%) was recrystallized from tetrahydrofuran to give (III), m.p. 155–156° (decompn., with darkening from 151°). NMR ($DCCl_3$, int. TMS): τ 7.35 (CH_3), τ 5.94 (CH_2), τ 5.47 (s, 5 Fc protons), τ 5.38 (t, 2 Fc protons), τ 4.97 (t, 2 Fc protons). The NMR of (II) hydrochloride was similar to this. IR: 1000, 1105, 535, 518, 500, 483, 334 cm^{-1}. (Found: C, 46.88; H, 5.25; Cl, 11.04; Fe, 16.81; N, 4.12. $C_{26}H_{34}Cl_2Fe_2N_2Pd$ calcd.: C, 47.04; H, 5.16; Cl, 10.68; Fe, 16.83; N, 4.22%.)

Complex (IV), M = Pd, X = Cl

A solution of 1.0 g of $K_2[PdCl_4]$ in 20 ml of water was added dropwise at room temperature to a stirred solution of 1.71 g of (II) hydrochloride in 20 ml of water. A yellow crystalline solid was obtained and washed with 3 × 10 ml of 0.05 *N* hydrochloric acid and 2 × 10 ml of diethyl ether to give 2.05 g (92%) of solid, m.p. 170–200° (darkens slowly). NMR: τ 7.36 (CH_3), τ 5.80 (CH_2), τ 5.66 (s, 5 Fc protons), τ 5.59 (m, 2 Fc protons), τ 5.42 (m, 2 Fc protons). The NMR of the other complexes of structure (IV) was very similar. IR: 1105, 1000, 515, 500, 483, 446, 338 cm^{-1}. (Found: C, 42.20; H, 4.87; Cl, 19.71; Fe, 14.94; N, 3.81; Pd, 14.31. $C_{26}H_{36}Cl_4Fe_2N_2Pd$ calcd.: C, 42.38; H, 4.93; Cl, 19.25; Fe, 15.16; N, 3.80; Pd, 14.48%.)

Complex (IV), M = Pt, X = Cl

In a similar manner $K_2[PtCl_4]$ gave a 72% yield of a yellow solid, m.p. 170–200° (slowly darkens). IR: 1105, 1000, 514, 500, 485, 450, and 330 cm^{-1}. (Found: C, 38.57; H, 4.72; Cl, 17.29; Fe, 13.63; N, 3.49; Pt, 24.05. $C_{26}H_{36}Cl_4Fe_2N_2Pt$ calcd.: C, 37.84; H, 4.40; Cl, 17.18; Fe, 13.53; N, 3.40; Pt, 23.66%.)

Complex (IV), M = Pd, X = CN

In a similar manner $Na_2[Pd(CN)_4]$ gave a 78% yield of yellow solid, m.p. 179–180°. IR: 2150, 2130, 1105, 1000, 514, 500, 485, 450, and 330 cm^{-1}. (Found: C, 51.34; H, 5.28; Fe, 16.20; N, 11.88; Pd, 15.06. $C_{30}H_{36}Fe_2N_6Pd$ calcd.: C, 51.54; H, 5.19; Fe, 15.98; N, 12.02; Pd, 15.17%.)

Complex (IV), M = Pt, X = CN

In a similar manner $Na_2[Pt(CN)_4]$ gave an 88% yield of solid, m.p. 175–177°. IR: 2140, 2130, 1105, 1000, 516, 503, 487, 450, and 400 cm^{-1}. (Found: C, 45.81; H, 4.64; N, 10.67. $C_{30}H_{36}Fe_2N_6Pt$ calcd.: C, 45.75; H, 4.61; N, 10.67%.)

Ligand replacement reaction with triphenylphosphine

In a typical experiment 0.2 g of (IV) (M = Pd, X = Cl) and 0.178 g of triphenylphosphine were placed in 4 ml of absolute ethanol and stirred at room temperature for 4 h. The resultant solid was collected and washed several times with ethanol and dried to give a quantitative yield of $[(C_6H_5)_3P]_2PdCl_2$ whose IR spectrum was identical to an authentic sample. Concentration of the filtrate *in vacuo* gave the hydrochloride of (II). (III) and the other samples of (IV) gave similar results.

Other reactions of (IV)

Reaction of (IV) (M = Pd, X = CN) with $Na[B(C_6H_5)_4]$ in water gave a solid identical with that obtained by reaction of (II) hydrochloride and $Na[B(C_6H_4)_4]$.

Reaction of (IV) with tetraphenylarsonium chloride in ethanol gave $(C_6H_5)_4As_2MX_4$ whose spectra were identical with known compounds.

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