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Preliminary communication

THE REACTION OF DICHLORO- AND DIIODO-(1,5-CYCLOOCTADIENE)-PLATINUM(II) WITH DIAZOMETHANE. A ROUTE TO BIS(HALOMETHYL)-PLATINUM(II) COMPLEXES

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Summary

Reaction of dichloro- and diiodo-(1,5-cyclooctadiene)platinum(II) with excess diazomethane affords the corresponding air-stable bis(halomethyl) complexes $Pt(CH_2X)_2(COD)$ (X = Cl or I) in excellent yield. Displacement of COD from $Pt(CH_2Cl)_2(COD)$ with 1,3-bis(diphenylphosphino)propane or two molar equivalents of PPh_3 gives the analogous phosphine complexes.

In the course of our studies [1, 2] of the reactions of diazomethane with palladium(II) and platinum(II) complexes, we have found that in the case of $Pt(COD)Cl_2$ and $Pt(COD)I_2$, carbene insertion into both metal halide bonds can be achieved. Reaction of the former with small aliquots of diazomethane in ether resulted in the build-up (TLC) of two products. These were purified by preparative TLC and crystallization and gave air-stable, colorless, solids. The structures of these complexes as 1, m.p. 123—126°C, and 2, m.p. 61—68°C, were readily assigned on the basis of their elemental analyses* and ^1H and ^{13}C NMR spectra. For compound 1, the ^1H NMR spectrum contains resonances attributable to a $PtCH_2Cl$ group (δ 3.97 ppm, $^1J(PtH)$ 74 Hz) and two sets of (magnetically non-equivalent) olefinic (δ 5.65 ppm, $^1J(PtH)$ 32 Hz and δ 4.88 ppm, $^1J(PtH)$ 75 Hz) and allylic (δ 2.70—2.25 ppm) protons. The ^1H NMR spectrum of 2, as anticipated, reveals only three resonances, one each for the chloromethyl (δ 3.84 ppm, $^1J(PtH)$ 60 Hz), olefinic (δ 5.34 ppm, $^1J(PtH)$ 40 Hz), and allylic protons. Compound 2, which was the only product formed when excess diazomethane was used, is stable as the solid or in solution in the absence of light or traces of acid. Treatment of $Pt(COD)I_2$ with an excess of

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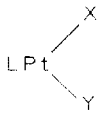
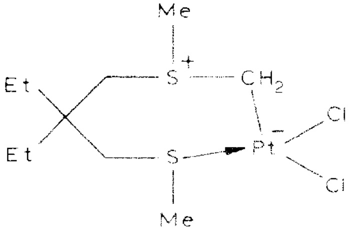
*All new compounds gave satisfactory elemental analyses.

diazomethane gave 3, which decomposes slowly when exposed to TLC on silica gel. Accordingly, it was purified by chromatography through a short plug of silica gel and then crystallization. The resulting colorless solid, which is again air-stable, had m.p. 109—112°C and gave ^1H and ^{13}C NMR spectra very similar to those of 2.



	L	X	Y
1	COD	Cl	CH_2Cl
2	COD	CH_2Cl	CH_2Cl
3	COD	CH_2I	CH_2I
4	DPPP	Cl	CH_2Cl
5	DPPP	CH_2Cl	CH_2Cl
6	$2PPh_3$	CH_2Cl	CH_2Cl



(7)

Displacement of COD from 1 and 2 is readily achieved by treatment with 1,3-bis(diphenylphosphino)propane at ambient temperature. The colorless, crystalline, products 4, m.p. 140—143°C, and 5, m.p. 189—192°C, gave ^1H, ^{13}C, and ^{31}P NMR spectra which allow their formulation as shown. For example, the ^{31}P NMR spectrum of the latter reveals a singlet (δ 0.99 ppm; external reference 25% TMP in C_6D_6, set at δ 141.38 ppm), with platinum satellites (^1J(PtP) 1829 Hz), while the spectrum of 4 contains two doublets (δ 1.69, −1.13 ppm; ^2J(PPtP) 23.5 Hz), each with platinum satellites (^1J(PtP) 4058, 1638 Hz, respectively). Both compounds are stable as solids or in acid-free solvents. Reaction of 2 with two molar equivalents of triphenylphosphine yielded 6, which is also an air-stable, colorless, solid, m.p. 120—135°C (decomp.). We have also attempted to displace COD from 2 with 2,2-dimethyl-1,3-bis(dimethylamino)propane and with 2,2-diethyl-1,3-bis(methylthio)-propane at ambient temperature. Perhaps not surprisingly, in light of the known [3] stability of $Pt(CH_3)_2(COD)$ to such conditions, the former did not react. Slow displacement did occur with the sulfide ligand to give polar products which have proved intractable. However, reaction of 1 with the same ligand gave a polar, very insoluble, solid which we tentatively formulate as 7 on the basis of elemental analysis and its ^1H NMR spectrum.

To our knowledge, compounds 2, 3, 4, and 6 constitute the first bis(halomethyl) complexes of platinum(II) reported. We are studying reactions of these compounds, including some aimed at their conversion into bimetallic species [4].

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4 See for example J.D. Scott and R.J. Puddephatt, Inorg. Chim. Acta, 89 (1984) L27.