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Preliminary communication

PHOTOLYSIS OF METHYL(TRIPHENYLPHOSPHINE)GOLD(I)

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Summary

Methyl(triphenylphosphine)gold(I) reacts with chloroform under UV irradiation to give methyl and solvent-derived radicals in triplet pairs showing CIDNP. An S_H2 substitution by methyl radicals at the gold centre is observed.

We previously described some bimolecular homolytic (S_H2) substitution reactions [3] at lead, tin, gold and platinum metal centres in which alkyl radicals were replaced by thermally generated benzoyloxy radicals. We now report the results of a study of the photolytic reaction of methyl(triphenylphosphine)gold(I) with chloroform, in which S_H2 substitution by methyl radicals at the gold(I) centre occurs as a side reaction.

When a solution of methyl(triphenylphosphine)gold(I) in $CDCl_3$ (0.02 mol l^{-1}) was irradiated*** in an NMR spectrometer**** a radical reaction took place, as was evident from the CIDNP [1] observed. Figure 1 shows the result of a multiscan experiment. The emissions and enhanced absorptions in the proton spectra, which are all due to net effects [4], are assigned as indicated in Table 1.

The most striking feature of the spectra is the emission polarization of $CH_3Au(PPh_3)$. The question arises whether or not this is due to a $CH_3^{\bullet}$ + $^{\bullet}Au(PPh)$ pair formed by photolytic homolysis. There are two reasons for not ascribing this effect to homolysis. Firstly, the emission of starting material is not observed in hydrocarbons; secondly, the sign of the polarization is the same as that of CH_3D and C_2H_6, which clearly are escape products. If homolysis contributed to the polarization of the starting material the sign

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***Light source was a Philips SP-1000 Hg lamp; the light was filtered through a solution of $NiSO_4$ in H_2O, then passed through a quartz light tube (diam. 8 mm) into the probe perpendicular to the sample tube.

****A Bruker WH-90-FT instrument was used with a pulse length corresponding to a flip angle of 40°.

TABLE 1

^{1}H NMR CIDNP SPECTRUM OF $CH_3Au(PPh_3)$ IRRADIATED IN $CDCl_3$

δ(ppm)	Mode^a	Assignment
0.20, triplet (J(HD) 2 Hz)	E	CH_3D
0.54, doublet (J(HP) 8.4 Hz)	E	$CH_3Au(PPh_3)$
0.86	E	C_2H_6 (weak)
2.06, triplet (J(HD) 0.9 Hz)	A	CH_3CDCl_2
2.21, 3.02, 3.83	A	unknown (weak)
2.32, 2.53	E	
2.72	A	CH_3CCl_3
5.28	A	$CDHCl_2$ (weak)
~7	N	$XAu(PPh_3)^b$

^{a} A = enhanced absorption, E = emission, N = normal. ^{b} X = CH_3, Cl.

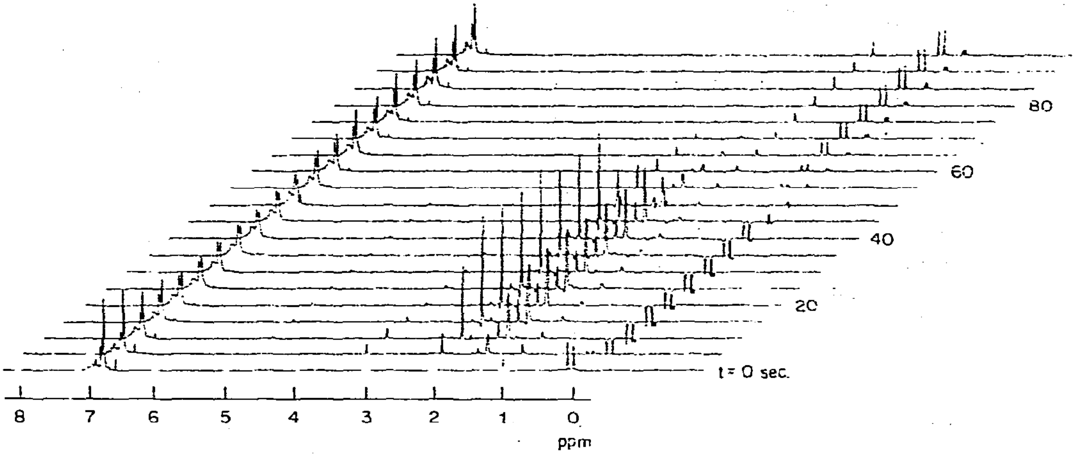

Fig.1. Series of NMR spectra taken during photolysis of 0.045 M $CH_3Au(PPh_3)$ in $CDCl_3$ at 28°C. Pulse interval 5 sec; one pulse (40°) per spectrum; light off at tenth pulse. The conversion is about 25 %. (Tho absorption at 1.5 ppm is assigned to H_2O).

of its polarization would be opposite to that of CH_3D because the latter is an escape product and the former a recombination product [4]. Therefore, it is proposed that the emission of $CH_3Au(PPh_3)$ is caused by polarized* escaping methyl radicals carrying out an S_H2 substitution at gold(I) according to eq. 1.

$$\widetilde{CH}_3{}^\bullet + CH_3Au(PPh_3) \rightarrow \widetilde{CH}_3Au(PPh_3) + CH_3{}^\bullet \qquad (1)$$

An alkyl radical substitution of this type has not been observed before for a transition metal compound.

The main products of the photolysis reaction are $Au(PPh_3)Cl$ (identified by its melting point) and CH_3D (identified from its NMR spectrum). The main reaction is a reaction between $CH_3Au(PPh_3)$ and $CDCl_3$. In the absence of further information we assume that $CH_3Au(PPh_3)$ is excited either to a singlet state which decays to an excited triplet state or excited to a triplet state. The latter reacts with the solvent to give $Au(PPh_3)Cl$ and the triplet radical pair $\overline{CH_3{}^\bullet + {}^\bullet CDCl_2}^{\,T}$ responsible for some of the polarizations observed. The methyl radicals mainly react with $CDCl_3$ to give CH_3D. The $^\bullet CCl_3$ radicals

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*$\widetilde{CH}_3{}^\bullet$ denotes a polarized methyl radical.

generated in this way in large quantity will form free encounter pairs (F) with methyl radicals. This leads to the following reaction scheme:

$$CH_3Au(PPh_3) \xrightarrow{h\nu} (CH_3Au(PPh_3)^S \longrightarrow)CH_3Au(PPh_3)^T \tag{2}$$

$$CH_3Au(PPh_3)^T + CDCl_3 \longrightarrow Au(PPh_3)Cl + \overline{CH_3{}^{\bullet} + {}^{\bullet}CDCl_2}^{\,T} \tag{3}$$

$$\overline{CH_3{}^{\bullet} + {}^{\bullet}CDCl_2}^{\,T} \longrightarrow \widetilde{CH_3}CDCl_2 \tag{4}$$

$$\widetilde{CH_3}{}^{\bullet} + CDCl_3 \longrightarrow \widetilde{CH_3D} + {}^{\bullet}CCl_3 \tag{5}$$

$$2\,\widetilde{CH_3}{}^{\bullet} \longrightarrow \widetilde{C_2H_6} \tag{6}$$

$$\overline{\widetilde{CH_3}{}^{\bullet} + {}^{\bullet}CCl_3}^{\,F} \longrightarrow \widetilde{CH_3}CCl_3 \tag{7}$$

The products of reactions 1, 5 and 6 show escape polarization, whereas those of reactions 4 and 7 show polarization of recombining radical pairs. Reactions 2 and 3 may be written differently, e.g. as an electron transfer (eq. 8):

$$CH_3Au(PPh_3) + CDCl_3 \xrightarrow{h\nu} [CH_3Au^{II}(PPh_3)]^+ + [CDCl_3{}^{\bullet}]^- \tag{8}$$

In view of the expected electronic properties of gold(II) atoms and the signs of the polarizations observed it is not likely that this radical ion pair would generate the CIDNP, although its occurrence cannot be excluded.

References

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