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The Photolysis of η^5-Cyclopentadienyltrimethylplatinum(IV)

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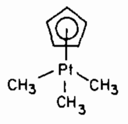
It was recently shown in this laboratory [1] that the initial reaction in the photolysis of η^5-C_5H_5-$W(CO)_3R$ ($R = CH_3CH_2C_6H_5$) is substantially, if not completely, dissociation of a CO group. Cleavage of the W–CH_3 bond appears to occur in coordinatively unsaturated η^5-$C_5H_5W(CO)_2CH_3$.

To ascertain how the absence of readily dissociable 2-electron neutral ligands such as CO influences the photochemistry of coordinatively saturated transition metal–alkyl complexes we turned to η^5-$C_5H_5Pt(CH_3)_3$ (*1*) [2]. This colorless compound with a 'piano-stool' structure [3] possesses unusually high thermal stability (*e.g.*, less than 1% decomposition in 75 min at 115 °C in toluene [4]). The presence of platinum(IV) therein, as well as the availability of platinum(II) as a stable oxidation state, enhance the possibility of occurrence of photochemically induced reductive coupling of two CH_3 groups. Other likely modes of photoreaction include homolysis of the Pt–CH_3 bond and α-hydrogen elimination [5].



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The electronic spectrum of *1* in cyclohexane is shown in Fig. 1; two absorption bands are observed at 254 ($\log \epsilon = 4.03$) and 289 nm ($\log \epsilon = 3.34$). Irradiations were carried out on carefully degassed solutions of *1* (generally 10^{-3} to 10^{-2} *M*) in hydrocarbon solvents (benzene, cyclohexane, methylcyclohexane, or cyclooctane) in quartz tubes with 300- or 350-nm lamps of a Rayonet Model RPR-100 reactor. Immediately the solutions turn yellow ($\lambda_{max} \sim 420$ nm) and gas is evolved. The quantum yield for the disappearance of *1* in $CH_3C_6H_{11}$ at 350 nm is 4.4×10^{-3}. On continued photolysis the yellow color of the solutions deepens, and then becomes yellow-brown and dark red-brown. Gas evolution slows considerably with time. If air is not rigorously excluded, metallic platinum precipitates from solution.

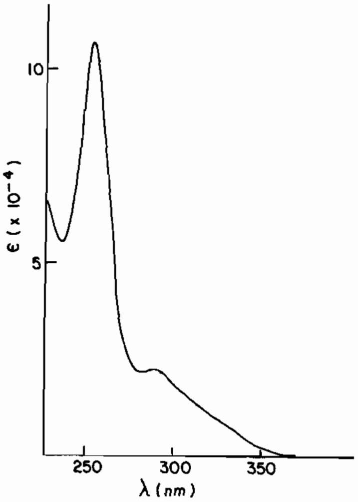

Fig. 1. Electronic spectrum of *1* (7.2×10^{-4} M) in cyclohexane at room temperature.

Irradiation of a benzene solution of *1* and phenyl N-tert-butyl nitrone in a quartz tube immediately leads to the appearance of an ESR signal characteristic of the $C_6H_5CH(CH_3)N(O)C(CH_3)_3$ radical [6]. Similarly, irradiation of *1* in the presence of nitrosodurene either in the Rayonet reactor (C_6H_6 solution) or in the cavity of an ESR instrument ($CHCl_3$ solution) immediately produces a signal of the CH_3 spin-adduct [7]. No signals are observed in the absence of the spin traps.

To obviate any possibility that the spin trap induces homolysis of the Pt–CH_3 bond during irradiation, a frozen solution of *1* in petroleum ether at liquid N_2 temperature was photolyzed in the cavity of an ESR instrument. Two signals were observed: one due to the CH_3 radical (quartet, $a_H = 22.5$ G) [8] and the other to an unidentified, probably Pt-containing species (~350-G broad signal at 2668 G, $g = 2.47$).

Gas chromatographic analysis of the gases above the photolyzed cyclooctane solution of *1* revealed the formation of methane (90 ± 1%), ethane (5 ± 1%) and ethylene (5 ± 1%). This composition appears to show little variation with the duration of photolysis up to 3 h, at which time evolution of gas is very slow. After 3 h, the collected gases corresponded to approximately one-third of the CH_3 ligands initially present in *1* that underwent photoreaction. Close to one-half of *1* remained unchanged and was recovered after thermolysis (*vida infra*). Thermal treatment (10–15 h, 55–77 °C) at this time of the photolyzed solution yielded metallic Pt, the gases CH_4, C_2H_6, and C_2H_4 (approximately 89:3:8), C_5H_6 and dimer (5%*), $CH_3C_5H_5$ and dimer (34%*), and unreacted *1*. By comparison, thermolysis of *1*

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*Based on reacted *1*.

in toluene has been reported [4] to give metallic Pt, CH_4, and 'relatively small amounts' of C_2H_6 and H_2.

To ascertain the origin of the hydrogen atoms in the methane formed during photolysis, deuterium-labeled η^5-$C_5H_5Pt(CD_3)_3$ (*1*-d_9) and η^5-$C_5D_5Pt(CH_3)_3$ (*1*-d_5) were prepared and irradiated under the conditions that mirrored those for *1*. The methanes collected during the photolysis of *1*-d_9 were shown by high resolution mass spectrometry to consist of 45% CD_4 and 55% CHD_3, whereas those formed during the photolysis of *1*-d_5 analyzed for 95% CH_4 and 5% CH_3D. In each case, there was little or no CH_2D_2. These results are explicable in terms of the CH_3 acquiring a hydrogen atom from other CH_3 groups (>45%), η^5-C_5H_5 (>5%), and solvent C_8H_{16} (<50%). Since isotopic selectivities, k_H/k_D, for the CH_3 radical attacking a given CH/CD are substantial (5.2–5.6 [9–11]), the relative contributions of the three sources of hydrogen atom cannot be determined more precisely from the above data alone. That the CH_3 picks up hydrogen originating from the CH_3 groups of other molecules of *1* (as contrasted with the hydrogen of the CH_3 groups of its own molecule) is illustrated by the results of the photolysis of 50:50 1:1-d_9. The methanes included CH_4 (43%), CH_3D (8%), CHD_3 (41%), and CD_4 (8%), the presence of CH_3D showing that CH_3 acquires deuterium from the CD_3 groups. The ethanes contained C_2H_6, $C_2H_3D_3$, and C_2D_6 in an approximate ratio 1:2:1.

The following conclusions may be drawn from the results of this investigation.

1) It has been shown unequivocally that irradiation of *1* leads to homolysis of the Pt–CH_3 bond:

$$\eta^5\text{-}C_5H_5Pt(CH_3)_3 \xrightarrow{h\nu} \eta^5\text{-}C_5H_5Pt(CH_3)_2\cdot + CH_3\cdot$$

Dissociation of a 2-electron neutral ligand, which often complicates the interpretation of data from photolysis of metal alkyl carbonyls and related complexes, does not enter into consideration in this case. There is no competing dissociation of C_5H_5 as evidenced by ESR spectroscopy. Moreover, α-hydrogen elimination and reductive coupling of methyl radicals occur to a negligible extent, if at all; this is shown by the virtual lack of formation of CH_2D_2 and by an approximate ratio 1:2:1 of the ethanes, C_2H_6:$C_2H_3D_3$:C_2D_6, in the aforementioned experiments with deuterium-labeled *1*.

2) The methyl radical picks up hydrogen with little selectivity in affording methane. This hydrogen originates from the CH_3 groups, η^5-C_5H_5, and solvent C_8H_{16}.

Experiments are under way to delineate various reactions following Pt–CH_3 bond homolysis and to identify Pt-containing species formed in the photolysis.

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