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Preliminary communication

RADICAL AND NON-RADICAL MECHANISMS OF REACTION OF BENZENETHIOL WITH TRANSITION METAL ALKYLS

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Summary

Benzenethiol reacts with methylgold(I) and methylplatinum(II) complexes to cleave the metal—carbon bond by a free-radical chain mechanism, but the similar, though much slower, reaction with methylgold(III) complexes proceeds by a mechanism not involving free radicals.

We wish to report an interesting duality of mechanism in reactions of alkyl-transition metal compounds with benzenethiol. The reactions 1—4 take place readily at room temperature and were easily followed by ^{1}H NMR spectroscopy in dichloromethane solution.

$$\mathrm{AuMeL + PhSH \rightarrow PhSAuL + CH_4} \quad (1)$$

$$\mathrm{AuMe_3L + PhSH \rightarrow \mathit{cis}\text{-}AuMe_2(SPh)L + CH_4} \quad (2)$$

$$\mathrm{\mathit{cis}\text{-}PtMe_2L_2 + PhSH \rightarrow \mathit{trans}\text{-}PtMe(SPh)L_2 + CH_4} \quad (3)$$

$$\mathrm{\mathit{trans}\text{-}PtMe(SPh)L_2 + PhSH \rightarrow \mathit{trans}\text{-}Pt(SPh)_2L_2 + CH_4} \quad (4)$$

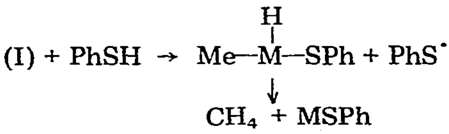
By allowing mixtures of alkyl-transition metal compounds to compete for a limited quantity of benzenethiol, the reactivity series $\mathrm{AuMe(PMe_3)} > \mathit{cis}\text{-}\mathrm{PtMe_2(PMe_2Ph)_2} > \mathrm{AuMe(PMePh_2)}, \mathrm{AuMe(PPh_3)} > \mathit{trans}\text{-}\mathrm{PtMe(SPh)(PMe_2Ph)_2} \gg \mathrm{AuMe_3(PMe_3)} > \mathrm{AuMe_3(PMePh_2)}$ could be determined.

The reactions involving the methylgold(I) and methylplatinum(II) compounds were totally inhibited on addition of the radical scavenger galvinoxyl and were accelerated on adding the radical initiator azobis(isobutyronitrile), AIBN, suggesting that they proceed by a free-radical chain mechanism, but reactions with the gold(III) compounds were not affected by the presence of galvinoxyl.

In the light of previous work [1—3] we have considered two mechanisms for the free-radical chain reactions, each of which involves attack of a thiyl radical on the alkylmetal (eqn. 5, $M = Au^{I}$ or Pt^{II}):

$$\mathrm{MeM} + \mathrm{PhS}^{\bullet} \rightarrow \underset{\text{(I)}}{\mathrm{Me\dot{M}SPh}} \qquad (5)$$

The intermediate (I) can then react in one of two ways:



$$\text{(I)} + \mathrm{PhSH} \rightarrow \mathrm{Me{-}\overset{H}{\underset{\downarrow}{M}}{-}SPh} + \mathrm{PhS}^{\bullet} \qquad \text{(A)}$$
$$\mathrm{CH_4} + \mathrm{MSPh}$$

$$\text{(I)} \rightarrow \mathrm{MSPh} + \mathrm{Me}^{\bullet} \xrightarrow{\mathrm{PhSH}} \mathrm{CH_4} + \mathrm{PhS}^{\bullet} \qquad \text{(B)}$$

In each case the thiyl radical produced continues the chain. That the reactions proceed at least in part by mechanism B, which involves an S_H2 reaction at the transition metal centre, was proved by the trapping of methyl radicals formed from the methyl-gold(I) and -platinum(II) compounds by t-BuNO and identifying the t-Bu(Me)NO$^{\bullet}$ radicals formed by ESR spectroscopy [4]. No radicals were trapped from the similar reaction with $\mathrm{AuMe_3(PMe_3)}$. However, t-BuNO, which is an efficient scavenger of methyl radicals but not of thiyl radicals [5], has little effect on the overall reaction rates suggesting that mechanism A (in which methyl radicals are never formed) predominates. In either mechanism the rate-determining step is likely to be that of eqn. 5, that is the rate of formation of (I), so that this step will determine the reactivity series given above. The intermediate (I) formed from $\mathrm{AuMe_3L}$ would be a gold(IV) compound, an unknown oxidation state of gold, perhaps explaining why a non-radical mechanism is preferred in this instance. In the case of the methyl-gold(I) and -platinum(II) compounds, the $\mathrm{Au^{II}}$ [6] and $\mathrm{Pt^{III}}$ [7] intermediates (I) should be readily formed, and the reactivity differences appear to be due largely to steric effects of the different phosphine ligands. It is interesting that the reactivity series is similar to the series of reactivity of alkyl-transition metal compounds towards oxidative addition reactions and reactions with alkenes, each of which may proceed by free-radical chain reactions [8,9].

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