

### Preliminary communication

---

## THE GENERALITY OF METAL ATOM-FREE RADICAL REACTIONS AND SYNTHESIS OF NEW TRIFLUOROMETHYLALKYLS OF GOLD(III) AND SILVER

M.A. GUERRA, T.R. BIERSCHENK and R.J. LAGOW\*

*Department of Chemistry, The University of Texas at Austin, Austin, TX 78712 (U.S.A.)*

(Received May 30th, 1985; in revised form February 26th, 1986)

### Summary

The cocondensation reaction of trifluoromethyl radicals with gold and silver vapors is an effective and efficient synthesis for the new compounds,  $\text{Au}(\text{CF}_3)_3$  and  $\text{AgCF}_3$ . Addition of trimethylphosphine to these alkyls yielded the room temperature stable compounds,  $\text{Au}(\text{CF}_3)_3\text{PMe}_3$  and  $\text{AgCF}_3(\text{PMe}_3)$ .

---

Further developments of importance on the synthetic concepts and procedures for synthesizing metal alkyls by the low temperature cocondensation of metal atoms with an excess of free radicals [1] have occurred. Extensive studies have provided growing evidence of the generality of this synthetic technique. It now appears that this reaction (Fig. 1), a reaction with very little activation energy, occurs easily and produces alkyls and  $\sigma$ -bonded compounds for all metals ranging from the Main Group metals, to transition metals, to even the actinide and lanthanide systems. This synthesis has been and will be the source of many novel classes of  $\sigma$ -bonded alkyl and other  $\sigma$ -bonded organometallic compounds for this procedure is a very effective technique for such compounds, using a wide variety of free radicals. Although there is ready formation of such alkyl species at low temperatures, a major problem is coping with the stability of the new alkyls. It is well known that major problems with alkyl stability are  $\beta$ -hydride elimination to form metal hydrides and metal-halide elimination for ligands containing halogens. These decomposition paths are particularly a problem for coordinatively unsaturated alkyls. We have found that almost all metal alkyls,  $\text{M}(\text{R})_n$  are stable, even if not isolable at low temperatures and certainly do not undergo decomposition at  $-196^\circ\text{C}$ . This is true also for coordinatively unsaturated alkyls when  $n$  is significantly lower than the coordination number for the highest or the most stable oxidation state.

A significant but lesser problem which plagues synthesis of alkyls from halogen-substituted radicals is the stripping of halide from the radicals by vapor contact with the high temperature metal atom species. We have found this generally to be an almost negligible problem except in the case of certain metals, specifically gold, silver and copper where this side reaction can preclude syntheses. An effective design for a reactor which has been successful in solving both the reactivity and stability problems is shown in Fig. 2a and 2b. Reactions in this system proceed with the synthetic strategy:

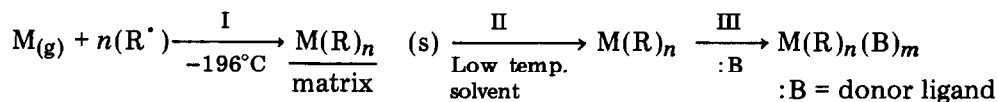


Fig. 1.

A metal is vaporized resistively or by electron beam bombardment from Site B onto a rotating thin-wall stainless steel cold finger (C) powered by a motor (E) and isolated with a  $10^{-10}$  torr rotating Ferroseal at Site D. At the same time, radicals are condensed on the opposite side (from Site A) using either radio frequency free radical generation (10 MHz-90 watts) [1] or by vacuum pyrolysis to yield (step I) a matrix of metal alkyls in excess radical recombination product (R-R). Under these conditions (I) at  $-196^{\circ}C$  even the most unstable metal alkyls are temporarily trapped and stabilized. If one warms the matrix of many transition metal alkyls and tried to do a vacuum transfer of the new compounds, immediate hydride or halide transfer would occur. Instead the reservoir H (in step II) is filled with a low temperature solvent (chlorofluorocarbons are used for alkyls of very low thermal stability). The solvent is admitted through a cannula. At this point the apparatus is rotated to a vertical position (Fig. 2b) so that the matrix containing the alkyl may be slightly warmed so that it slides off cold surface C in the form of an ice and falls directly into the solvent in reservoir H. H is maintained at a very low temperature (perhaps  $-120^{\circ}C$  initially) and is never allowed to warm over the threshold decomposition temperature of the coordinatively unsaturated alkyl under study. Such hydrocarbon and halocarbon alkyls are so thermally unstable that contact with the walls of the apparatus during the dropping procedure will result in substantial decomposition. Thus the rotating pivot vacuum line reactor system is an effective but not necessarily unique method for preserving these unstable species and assuring that the matrix not be warmed until the new species is solvated.

Should the new compound at the end of step II be a coordinatively unsaturated transition metal species with a less than 18 electron count, it is not usually isolable at room temperature without base stabilization. However, at this stage one can transfer with a refrigerated cannula the solvated metal species into an NMR tube and at low temperature, observe by NMR very accurately and precisely the temperature and rate of decomposition of such exotic species. Although the compounds selected for illustration in this manuscript are more stable, we have handled transition metal compounds decomposing as low as  $-120^{\circ}C$  successfully.

In step III (Fig. 1) a base (ligand) is added by vacuum transport or injected through the cannula to the stirred reservoir H which is cooled with a dewar

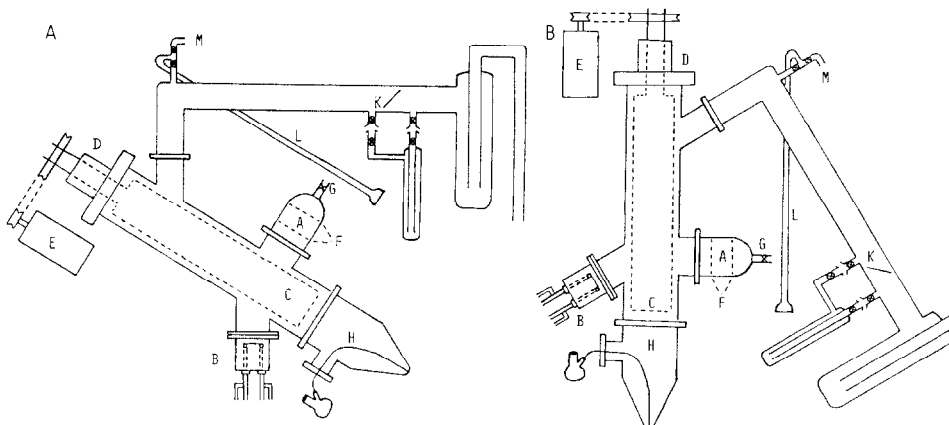


Fig. 2. (A) Rotating cold finger reactor (position I); (B) rotating cold finger reactor (position II).

flask. The reactants are slowly warmed until a base stabilized complex of the form  $M(R)_n(B)_m$  is obtained. Such species are usually crystalline after stabilization with bases selected to produce an 18 electron molecule. New compounds are obtained rather pure and this procedure for most transition metal species usually results in rapid access to single crystals. It should not be overlooked that the intermediate (unsaturated alkyl) at the end of stage II can be a very interesting and reactive reagent.

An important feature with respect to minimizing vapor contact with halocarbon radicals in the gold, silver and copper systems is the fact that metal vapor inlet B is located exactly opposite without subtending the base of inlet A. The value of these procedures are obvious since many unstabilized transition metal alkyls decompose at temperatures significantly below  $-20^\circ\text{C}$  where the efficacy of organolithium reactions with metal halides are so reduced kinetically as to preclude reaction. Certainly  $\beta$ -hydride elimination or halide transfer to the metal would occur as rapidly as these species formed.

Using this procedure, the unstable compounds  $\text{Au}(\text{CF}_3)_3$  and  $\text{AgCF}_3$  are generated and trimethylphosphine was used to stabilize these species to give the new crystalline compounds tris(trifluoromethyl)(trimethylphosphine)gold and trifluoromethyl(trimethylphosphine)silver. The gold and silver alkyls are of interest themselves, but they also illustrate both types of problems which this reaction system was designed to overcome.

Gold metal (0.1619 g) was vaporized and cocondensed at  $-196^\circ\text{C}$  with an excess of trifluoromethyl radicals (generated from hexafluoroethane) over a 2 h period. The frozen matrix was dropped from the cold finger and was slowly warmed to  $-80^\circ\text{C}$  to allow the unreacted hexafluoroethane to vacuum distill from the reactor. Ten milliliters of  $\text{CH}_2\text{Cl}_2$  and one milliliter of  $\text{PMe}_3$  were then condensed in the reservoir at  $-196^\circ\text{C}$ . The solution was stirred at  $-78^\circ\text{C}$  for a few minutes and warmed to room temperature before the volatiles were removed. Extraction with  $\text{CH}_2\text{Cl}_2$  in a dry box gave  $\text{Au}(\text{CF}_3)_3 \cdot \text{PMe}_3$  (0.0779 g) in 20.2% yield. Vacuum sublimation at  $70^\circ\text{C}$  yielded pure colorless crystals of  $\text{Au}(\text{CF}_3)_3 \cdot \text{PMe}_3$  (m.p.  $126\text{--}127^\circ\text{C}$ ). Fluorine NMR in  $\text{CD}_2\text{Cl}_2$  gave a singlet and a doublet at 30.5 and 32.3 ppm downfield from external  $\text{CFCl}_3$ , respective-

ly. The integration showed a 2/1 ratio of the singlet to the doublet. The  $^{19}\text{F}$  NMR is consistent with a square planar arrangement comprised of two equivalent *cis*- $\text{CF}_3$  (singlet) and a *trans*- $\text{CF}_3$  (doublet  $J(\text{P}-\text{F})$  81.3 Hz) which was split by the phosphorus atom. A structure determination is underway. The  $^1\text{H}$  NMR in  $\text{CD}_2\text{Cl}_2$  contained methyls at  $\delta$  1.8 ppm from external TMS which were split into a doublet ( $J(\text{P}-\text{H})$  5.6 Hz). The mass spectrum gave  $\text{Au}(\text{CF}_3)_2 \cdot (\text{CF}_2) \cdot \text{PMe}_3$  6% (P-F),  $\text{Au}(\text{CF}_3)_2 \cdot \text{PMe}_3$  (47%) and other fragments. A high resolution mass spectrum confirmed the parent minus fluorine peak; calculated 461.9969 amu, measured 461.9986 amu (3.7 ppm error).

Alternatively the homoleptic unstabilized alkyl can be studied without complexing with phosphine by low temperature  $^{19}\text{F}$  NMR ( $-80^\circ\text{C}$  cannula transfer by pressurizing the reactor with Ar). At  $-80^\circ\text{C}$ ,  $\text{Au}(\text{CF}_3)_3$  gave a singlet at 39.6 ppm from  $\text{CFCl}_3$ . This was the only peak observed in the  $\text{M}-\text{CF}_3$  region. Subsequent incremental temperature studies showed that gold fluoride began to form at  $0^\circ\text{C}$ .

Additionally, 0.1522 g of silver vapor was generated and condensed with trifluoromethyl radicals in a manner similar to the gold reaction. The  $\text{AgCF}_3$  formed was treated with trimethylphosphine to obtain 0.0864 g (24.2% yield) of trifluoromethyl(trimethylphosphine)silver. Then  $\text{AgCF}_3 \cdot \text{PMe}_3$  was sublimed under vacuum to yield a white solid which was light sensitive. The  $^{19}\text{F}$  NMR gave a doublet in  $\text{CD}_2\text{Cl}_2$  at 31.5 ppm ( $J(\text{Ag}-\text{F})$  40.7 Hz) from external  $\text{CFCl}_3$ . The  $^1\text{H}$  NMR showed a doublet at 1.3 ppm ( $J(\text{Ag}-\text{H})$  2.1 Hz) for the methyls. A  $^{31}\text{P}$  NMR gave a broad singlet at 37.6 ppm downfield from external  $\text{H}_3\text{PO}_4$ . A mass spectrum produced the silver isotope pattern (P-F)  $\text{AgCF}_2 \cdot \text{PMe}_3$  (3.5%) along with the expected fragments. A high resolution mass spectrum confirms the parent minus fluorine peak using the 107 silver isotope; calculated 232.9458 amu, measured 232.9464 amu (2.5 ppm error).

Alternatively at  $-80^\circ\text{C}$ , one can study the unstabilized  $\text{AgCF}_3$  by  $^{19}\text{F}$  NMR and observe a doublet at 32.3 ppm ( $J(\text{Ag}-\text{F})$  33.9 Hz) from external  $\text{CFCl}_3$ . This intermediate was a bit less stable than the gold system and silver fluoride began to form at  $-10^\circ\text{C}$ . If the reactions are attempted in a more conventional style metal atom reactor where metal vapor is allowed to mix with the ligand or radicals in the gas phase, the quantities of metal alkyls are so small that no metal alkyls can be isolated.

Previous work on trifluoromethyl-substituted alkyls has concerned reactions of trifluoromethyl iodide [2]. Johnson and Puddephatt have studied the reaction of  $\text{CH}_3\text{Au} \cdot \text{PMe}_3$  with  $\text{CF}_3\text{I}$  to obtain  $\text{AuCF}_3 \cdot \text{PMe}_3$  [3]. Klabunde and coworkers have cocondensed silver atoms with  $\text{CF}_3\text{I}$  to form a matrix that when hydrolyzed produced  $\text{CF}_3\text{H}$  which hinted the formation of trifluoromethyl silver [4].

These developments demonstrate capabilities for solving important problems in transition metal chemistry.

**Acknowledgement.** We are grateful for support of this work by the Air Force Office of Scientific Research (AFOSR-82-0197), the National Science Foundation (CHE-8210708) and the Robert A. Welch Foundation (F-700).

## References

- 1 T.J. Juhlke, R.W. Braun, T.R. Bierschenk and R.J. Lagow, *J. Am. Chem. Soc.*, 101 (1979) 3229.
- 2 R.N. Haszeldine and B.O. West, *J. Chem. Soc.*, (1956) 3631.
- 3 A. Johnson and R.J. Puddephatt, *J. Chem. Soc., Dalton Trans.*, (1976) 1360.
- 4 K.J. Klabunde, *J. Fluorine Chem.*, 7 (1976) 95.