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MECHANISM AND UTILITY OF THE DIRHENIUM DECACARBONYL CATALYZED FORMATION OF SILYL ETHERS

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Abstract: A mechanism for dirhenium decacarbonyl catalyzed formation of silyl ethers is proposed. This reaction is a good alternative to the standard silylation procedure involving the use of more expensive silyl chlorides; even tertiary silyl ethers are readily formed.

During the course of ongoing research it became necessary to prepare monoalkoxysilane derivatives. Although it is feasible to prepare this type of compound *via* monochlorination of the silane[1] and subsequent displacement with an alcohol, we were more interested in a one step conversion. Many catalysts are known to promote the silylation of alcohols[2,3], however, only two publications have addressed the reaction outlined in equation 1[3]. Since these report unsatisfactory yields of the desired monoalkoxy derivative, we embarked on the search for a homogeneous catalyst to effect this transformation.

$$RSiH_3 + R'OH \xrightarrow{\text{catalyst}} RH_2SiOR' + H_2 \qquad (1)$$

Of the complexes investigated[4], dirhenium decacarbonyl proved to be the most effective, affording approximately 90% of the desired monoalkoxyphenylsilane derivative. Although a mechanism has been proposed for the dimanganese decacarbonyl catalyzed reaction[5] (scheme 1), the silicon activation step is ambiguously based on the Chalk and Harrod mechanism for dicobalt octacarbonyl[6]. Firstly, $Co_2(CO)_8$ is susceptible to a facile, thermal CO dissociation while both $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ act as efficient catalysts only under photochemical conditions (see below). Secondly, in this mechanism, oxidative addition of the silane would occur to the coordinatively unsaturated metal centre after CO dissociation. Reductive elimination of $HMn(CO)_5$ would follow with concomitant formation of $R_3SiMn(CO)_5$, after CO uptake. With $Re_2(CO)_{10}$, we have demonstrated that the rhenium hydride species is not involved in the catalytic cycle (*vide infra*).

$$M_2(CO)_{10} + R_3SiH \longrightarrow R_3SiM(CO)_5 + HM(CO)_5$$

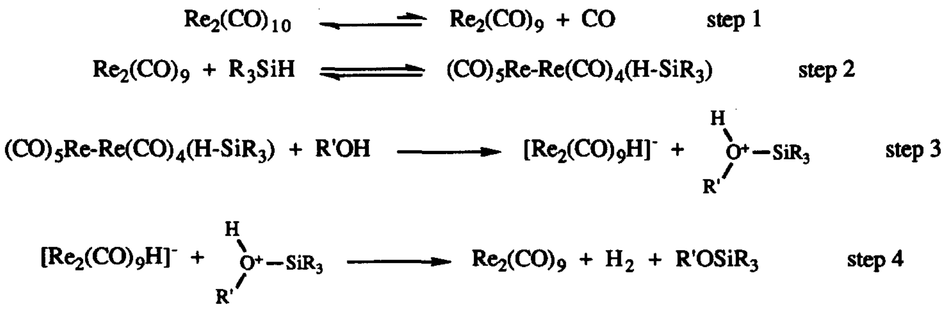
$$HM(CO)_5 + R_3SiH \longrightarrow H_2 + R_3SiM(CO)_5$$

$$R_3SiM(CO)_5 + R'OH \longrightarrow R_3SiOR' + HM(CO)_5$$

Scheme 1

A major proportion of the chemistry of $M_2(CO)_{10}$ (where M = Re or Mn) involves the photochemically induced, homolytic dissociation of the M-M bond, with subsequent formation of $\cdot M(CO)_5$ radicals[7]. In light of this, it has been proposed that there is a hydrogen atom transfer from the silane to this radical[8]. On the basis of Si-H and M-H bond energies[9], this is not a thermodynamically favorable process. If, however, this metal hydride were to be involved in the catalytic cycle, replacing the $M_2(CO)_{10}$ catalyst with this compound, should facilitate a reaction of at least the same rate. Thus, a sample of $HRe(CO)_5$ was prepared, according to a literature procedure[10]. On subjecting the reaction to this catalyst, the rate was retarded, complete reaction taking 1 hour, ie four times longer than the standard reaction. Furthermore, it has been shown that O_2 has a dramatic retarding influence on reactions involving $\cdot Re(CO)_5$ radicals[11].When our standard reaction was saturated with oxygen and the reaction performed under an oxygen atmosphere, no rate effect was noted.

We now propose the mechanism[12] outlined in scheme 2. We believe that the photochemical process occurring in this reaction is the dissociation of CO (step 1) to form a coordinatively unsaturated metal centred species, the active catalyst. This species then forms an addition complex with the silane (step 2), polarizing the Si-H bond and rendering the silicon atom susceptible to a facile nucleophilic attack (step 3).



Scheme 2

Thus, there is no reaction, even after several days, when the process is carried out in the total absence of light. If a phenylsilane solution of $Re_2(CO)_{10}$ is photolyzed and the alcohol added to this reaction mixture in the absence of light, reaction occurs with a rate equal to the standard reaction. When performed under a CO atmosphere, there is a 15 minute induction period prior to H_2 evolution. The use of nmr (^{29}Si, ^{1}H and ^{13}C) was uninformative. The only compounds observed were starting materials and products. On studying the reaction by infrared, we observed no additional absorptions for the reactive intermediates, hence, we propose an equilibrium for steps 1 and 2, lying well over to $Re_2(CO)_{10}$. Evidence for this equilibrium was observed when the reaction was performed under a 35-40 mmHg vacuum. A solution of the catalyst and silane was placed under vacuum and irradiated with a tungsten lamp for 30 minutes. The reaction flask was placed in the dark and, after a further 2 hours, an atmospheric pressure of argon was introduced. This was allowed to stand for a further 36 hours before the alcohol was added. A 52% conversion to the silyl ether was observed after 8 minutes while, after 12 minutes, only a 17% conversion was observed in the blank reaction. Recent publications by Brown *et al.*[13]also offer corroborative evidence for this type of equilibrium in the $Mn_2(CO)_{10}/Et_3SiH$ system. Furthermore, rhenium carbonyl addition complexes, similar to the one proposed, have been isolated and fully characterized[14].

The reaction shows a dramatic solvent dependency (Table 1). The reaction time increases in the order of increasing solvent polarity: no solvent > pentane > cyclohexane > CH_2Cl_2 > benzene > ^{t}butylmethylether. This provides further support for the proposed mechanism. Polar solvents can compete more effectively for the vacant site on the active catalyst. They are also able to solvate the polarized/ionic intermediates more readily, hence retarding the reaction.

Run	Solvent	Reaction Time*
1	no solvent	40 mins
2	pentane	2 hrs
3	cyclohexane	4 hrs
4	dichloromethane	8 hrs
5	benzene	20 hrs
6	^{t}BuMe-ether	>24 hrs**

Table 1: * These reactions were performed under normal laboratory lighting using neopentyl alcohol and phenylsilane. **75% conversion and several unidentified side products were observed with the use of this solvent after 24 hrs.

The rate determining process could be a) CO dissociation step, 1; b) formation of the silane addition complex, step 2; c) nucleophilic displacement by the alcohol, step 3. CO dissociation is discounted as the rate determining step since the reaction is retarded when phenylsilane is replaced with triethylsilane. If step 3 is rate determining, the reaction time would vary significantly with different alcohols and this was not observed. The reaction times were essentially the same when phenol, ^{t}butanol and neopentyl alcohol were used in conjunction with triethylsilane. Thus, we believe step 2 to be rate determining, the reaction being retarded by sterically more demanding silanes.

In conclusion, we believe the mechanism outlined in scheme 2 to be the most probable. Dirhenium decacarbonyl is an excellent catalyst for this reaction, even tertiary alcohols react efficiently. Phenols are also readily transformed to silyl ethers, unlike dicobalt octacarbonyl catalysis[6]. The turnover number for $Re_2(CO)_{10}$ is >6000 while that for $Mn_2(CO)_{10}$ is approximately half that. Although we have not studied the dimanganese decacarbonyl catalyzed reaction in the same depth, it is reasonable to assume that the catalytic cycle is the same.

Standard Reaction: Neopentyl alcohol (180mg, 2.0mmol) and dirhenium decacarbonyl (20mg, 1.5mol%) were added to phenylsilane (1ml, 4 equiv.) under an argon atmosphere and this solution was photolyzed with a 200W tungsten lamp, at a distance of 6-8 inches, until hydrogen evolution ceased (15 minutes). The reaction mixture was analyzed by GC, GCMS and nmr (^1H and ^{13}C). The ratio of products were typically 86-88% monoalkoxysilane and 12-14% dialkoxysilane, the reaction being quantitative in alcohol.

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