in the geometries of the $(SbCl_6)^{-1}$ and $(SbCl_6)^{-3}$ complex ions. Generally, only totally symmetric vibrations are resonance enhanced. The observed resonance enhancement of the T_{2g} Cl-Sn-Cl deformation and the combination band involving T_{2g} and E_g symmetry modes (Table I) suggests that the F_{m3m} selection rules, which apply to the pure Cs_2SnCl_6 lattice, are removed in the doped compounds.

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Chemistry of Transition Metal–Phosphine and –Phosphite Complexes. 1. Photochemical Substitution Reactions of Tetrakis(triphenyl phosphite)cobalt(I) Hydride

Sir:

Trialkyl and triaryl phosphite stabilized cobalt hydrides have been shown to be relatively inert to phosphite substitution reactions.[1-3] The substitution of a phosphite ligand in general requires long reaction times (1-6 weeks), elevated temperatures (~100 °C), and/or elevated pressures (1-10 atm of CO) with resulting low yields.

During the course of our studies on the chemistry of $HCo[P(OC_6H_5)_3]_4$ we have found that this complex undergoes facile ligand substitution reactions when irradiated with 340-nm light in the presence of another ligand according to

$$HCo[P(OC_6H_5)_3]_4 + L \xrightarrow{h\nu} HCo[P(OC_6H_5)_3]_3L + P(OC_6H_5)_3 \quad (1)$$

Good yields have been obtained in relatively short reaction times. The substitution of the first $P(OC_6H_5)_3$ was found to be essentially complete after only 20-min photolysis.[4] Typically, for L = CO, a solution of 9.7 g (7.35 mmol) of $HCo[P(OC_6H_5)_3]_4$ in 300 mL of tetrahydrofuran (THF) was purged with CO for 5 min. The solution was then irradiated with a 450-W Ace-Hanovia immersion lamp for 20 min while the CO bubbling was maintained. Vacuum removal of the THF and a benzene-*n*-propanol recrystallization afforded 6.0-6.5 g (83-90% theoretical) of pure $HCo[P(OC_6H_5)_3]_3CO$.[5] Yields of monosubstituted products where L = phosphite were in general slightly lower. Shorter photolysis times left unreacted $HCo[P(OC_6H_5)_3]_4$, while longer reaction times produced less of the desired $HCo[P(OC_6H_5)_3]_3L$ products.

Infrared analysis of the reaction mixture, where L = CO, photolyzed for several hours indicated the presence of significant amounts of $HCo[P(OC_6H_5)_3]_2(CO)_2$ and $[Co(CO)_3P(OC_6H_5)_3]_2$. Indeed, both of these complexes were isolated in significant yield from the reaction mixture any time the photolysis exceeded 1 h. The substitution of the second phosphite to form the $HCoL_2L'_2$ complexes was found to proceed far more slowly than the substitution of the first phosphite under identical conditions. These observations indicated to us that the photochemical substitution process, for L = CO, was proceeding stepwise according to Scheme I. The tricarbonyl hydride, $HCo(CO)_3P(OC_6H_5)_3$, has been reported[6] to decompose rapidly above 0 °C to form H_2 and $[Co(CO)_3L]_2$ analogous to the thermal decomposition[7] of $HCo(CO)_4$ to produce H_2 and $[Co(CO)_4]_2$.

Scheme I

$$HCoL_4 + CO \xrightarrow{h\nu} HCoL_3CO + L$$
$$\xrightarrow[h\nu]{+CO} HCoL_2(CO)_2 + L \xrightarrow[CO]{h\nu} HCoL(CO)_3 \longrightarrow [CoL(CO)_3]_2$$

Scheme II

$$HCoL_4 + S \overset{h\nu}{\rightleftarrows} \text{“}HCoL_3S\text{”} + L \underset{-L'}{\overset{+L'}{\rightleftarrows}} HCoL_3L' + S$$

The monocarbonyl was found to be photochemically inert to the substitution of the CO by phosphite, even in the presence of a 10-fold excess of phosphite. Thus, it appears that reaction 1, for L = CO, is photochemically as well as thermally[3] irreversible. Consequently, when $HCo[P(OC_6H_5)_3]_3CO$ was photolyzed as described above, but in the absence of added substrate, essentially quantitative recovery of $HCo[P(OC_6H_5)_3]_3CO$ occurred. Preliminary studies indicate that for L = phosphite, reaction 1 is photochemically reversible and the reaction rate is independent of the amount of added phosphite. This implies that ligand dissociation to form the coordinatively unsaturated "$HCoL_3$" intermediate is the rate-determining step as shown in Scheme II. It is quite likely that the coordinatively unsaturated intermediate "$HCoL_3$" exists as a THF solvate, "$HCoL_3$-THF", analogous to the known acetonitrile complex $HCo[P(OC_6H_5)_3]_3(CH_3CN)$.[8] Infrared analysis of the reaction mixture produced when $HCo[P(OC_6H_5)_3]_4$ is photolyzed in a 50:50 THF-CH_3CN mixture under nitrogen, followed by bubbling with CO, shows the presence of both the monocarbonyl and dicarbonyl substitution products. This can be taken to indicate the presence of a solvated intermediate "$HCoL_3$-solvate" in the ligand substitution process. However, it does not entirely rule out the possibility of an ortho-metalated intermediate.[1] The failure of our attempts to isolate the solvated complex is probably due to the presence of the liberated phosphite, which is known to rapidly displace acetonitrile from $HCoL_3(CH_3CN)$ complexes to form $HCoL_4$.[8]

The synthetic utility of this very interesting photochemical reaction warrants further study. Studies directed along these lines as well as at establishing the nature of the purported intermediate are currently in progress in our laboratories.

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