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NOTE

CRYSTAL AND SOLVENT EFFECTS IN THE NITROGEN COMPOUND OF COBALT, $HCo(N_2)[(C_6H_5)_3P]_3$

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Effects of substituent R on the $\nu(N_2)$ frequency in the nitrogen complex of cobalt, $HCo(N_2)(PR_3)_3$ (R=alkyl or aryl) have been described recently[1,2]. Several studies have been reported[3-10] on the compound, $HCo(N_2)[(C_6H_5)_3P]_3$, since its first isolation by Yamamoto *et al.*[3] and more recent X-ray studies[11,12] seem to have finally resolved the conflicting reports regarding its structure.

We have made certain interesting observations concerning the solvent and crystal effects which lead to the formation of two forms of the same compound differing only in the observed IR frequencies of the coordinated (N_2) molecule. In solution, both forms show a sharp band at 2085–2095 cm^{-1} due to $\nu(N_2)$. In the solid state, however, one of the forms exhibits one band at 2086–2089 cm^{-1} whereas the other form shows two sharp bands of very nearly equal intensity at 2084.5 and 2101 cm^{-1}. Indeed some previous workers[9-12] have come across these two forms of the compound during the course of their preparations but until now no detailed studies seem to have been carried out to throw light on the causes and the conditions under which one or the other form is obtained. The analytical results for both forms are the same and perhaps the molecular structure of the solid compound with one $\nu(N_2)$ band (not studied) is the same as that of the form with two bands as studied by Ibers *et al.*[11,12] using X-ray analysis.

We have carried out extensive studies to explore the conditions under which one form or the other predominates in the preparations. Effects of variables like reaction temperature, solvent employed and the conditions of recrystallization have been studied. Indeed, we have been able to characterize more or less the precise conditions under which it is possible to isolate one form of the compound without contamination with the other. The two forms differ only in their IR spectra. Table 1 summarises the results obtained.

When freshly crystallized and dried only for a short period the compound contains the solvent but upon drying under vacuum for 3 to 4 hours, the solvent-free form is obtained. Solvated or solvent-free, the form with two bands always shows both these bands in its spectrum. This outrules the possibility that the splitting of the

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TABLE I

PREPARATION AND IR SPECTRA OF THE COMPOUND $HCo(N_2)[(C_6H_5)_3P]_3$ OBTAINED UNDER DIFFERENT EXPERIMENTAL CONDITIONS

Expt.	Reaction			IR spectra (cm^{-1})				Remarks
	Ratio Co/Al/PPh$_3$	Solvent	Temp. (°C)	Solution (aliquot from reacn. mixture)	Solid			
					Ppt. obtained from reacn. mixture	Solvent and temp. of recrystallization	Recryst. product	
1 2	1/1/3 1/3/3	Ether	25	2090	2085, 2101 (N≡N), 535 (Co–N) (KBr)	Ether; 0°	2085, 2101, 535 (KBr)	No difference observed upon adding (iso-$C_4H_9)_3Al$ in excess
3	1/1/3	Ether	−10 to +5	2089		Ether; −80°	2084, 2100, 535 (KBr)	
						Toluene; 0°	2088.5 (KBr)	
4	1/3/3	Ether	−10		2084.5, 2101, 540 (KBr)			
5	1/1.2/3	Ether	25	2090	2084.5, 2101, 540 (KBr)	Ether; 0°	2084.5, 2101, 540 (KBr)	Compound prepared by passing H_2 and then N_2 (via the hydride)
6	1/1.2/3	Pentane	−10	2095		Pentane; 0°	2084.5, 2101 (vaseline), 2084.5, 2101, 540 (KBr)	
7	1/1.2/3	Pentane	25	2095	2084.5, 2101, 540 (KBr)	Pentane; 25°	2087, 540 (KBr)	Very small shoulder at 2100 cm^{-1} in spectra of recryst. product; no difference observed upon adding excess PPh$_3$ or (iso-$C_4H_9)_3Al$
8	1/2/6	Pentane	25	2095	2084.5, 2101, 540 (KBr)	Pentane; 25°	2086.5, 540 (vaseline), 2087, 540 (KBr)	
9	1/1/3	THF	25	2089	2085, 535 (vaseline), 2086, 535 (KBr)	THF; 25°	2086, 538 (KBr)	
10	1/1/3	Benzene	25	2088				
11	1/1/3	Toluene	25	2088		Toluene; 0°	2089, 540 (KBr)	
12	1/1/3	Toluene	0	2088		Toluene; −80°	2089, 540 (KBr)	

bands is due to the solvent content in the compound[11]. Also, none of these bands could be assigned to the Co–H frequency as proposed earlier[11]. This was confirmed by the results of Sacco *et al.*[10] who prepared the deuterated species $DCo(N_2)[(C_6H_5)_3P]_3$ still showing the same two bands. We propose that this splitting of the bands is due to a crystal effect in the compound. Further support for this conclusion is provided by the fact that in solution one always observes only one band (the molecular species).

The data presented in Table 1 though extensive are not entirely conclusive. There are certain subtle conditions for the formation of one form or the other and these cannot be exactly pinpointed. However, certain conclusions can be drawn: (*i*) The compound when prepared and crystallized from THF, toluene or benzene shows one band at 2086–2089 cm^{-1}. (*ii*) When the reaction is carried out at room temperature in pentane, a precipitate is obtained which shows two bands. However, upon letting the supernatant liquid of the reaction mixture stand for some time, another crop of crystals is obtained which shows only one band. The fact that the same experiment in pentane gives both forms could perhaps be attributed to the subtle differences of conditions under which the precipitation or the recrystallization of the compound occur (agitation of the mixture, difference in solubility of the two forms, etc.). It may also be suggested that since the form with two bands is more stable (*vide infra*), this precipitates out first in spite of the agitation of the mixture whereas the form with one band necessitates standing of the solution undisturbed for a while. (*iii*) From ether, always the form with two bands is obtained.

The solvent effect can further be illustrated from the following and similar other observations. When the form with two bands (obtained from ether) was dissolved in toluene or benzene and recrystallized by cooling, the form with one band was obtained. It would imply once again that in solution only one molecular species exists. During crystallization, this rearranges into two different forms depending upon the solvent.

Another interesting observation made by us was that under certain conditions, the form with one band upon slow heating at 40–60° transforms into the compound with two bands. The compound recrystallized from toluene (one band, 2089 cm^{-1}) for example, was heated slowly (in the form of a pressed KBr disc as well as by itself) and its spectra recorded. After a few minutes of heating, two shoulders near 2100 and 2085 cm^{-1} began to show up and the intermediate peak at 2089 cm^{-1} began to disappear slowly. Before the compound could decompose finally, there were two sharp bands at 2101 and 2084.5 cm^{-1} and the intermediate peak had almost disappeared. The form with two bands is more stable. This transformation is not reversible. An additional sharp band at 535–540 cm^{-1} in the solid state for both the forms was observed by us. This was not reported by earlier workers. It may be assigned to the $Co–N_2$ mode by analogy to $Ru–N_2$[13] and $Os–N_2$[14] described earlier. A similar band near 500 cm^{-1} assignable to Co–N vibration is observed in the case of cobalt ammine complexes. However, the assignment is tentative and if finally confirmed by further measurements would demonstrate the strong metal–nitrogen coordination in the compound.

We have also studied an interesting reaction of the compound with methyl iodide producing a green crystalline product. The details would be published in a later communication.

EXPERIMENTAL

Two different routes were employed for the preparations as described separately by Yamamoto *et al.*[3] and Misono *et al.*[5,6]. We found that the reaction was 2 or 3 times faster if cobalt(II) acetylacetonate was used instead of the cobalt(III) acetylacetonate as a starting material. Triisobutylaluminum was used as the reducing agent in all the cases.

Details of a typical preparation were as follows. Cobalt(III) acetylacetonate (5 mmole, 1.58 g) and 15 mmole (3.94 g) of triphenylphosphine were transferred along with 120 ml of pure dry ether into a reaction flask equipped with a three-arm assembly, one of the necks being fitted with a self sealing rubber cap. The apparatus was purged with dry oxygen-free nitrogen for 2 h. The temperature of the mixture was adjusted as required (*vide* Table 1) using a suitable bath. Triisobutylaluminum (1.5 ml) was added dropwise using a hypodermic syringe while keeping the mixture continually stirred. After 1–3 h (depending upon the temperature; the reaction is slower at low temperatures) the suspension dissolved giving a clear deep orange solution. Finally an orange precipitate began to appear slowly and in a few minutes the precipitation was complete. This precipitate was filtered off, washed with a little ether and dried under nitrogen (*cf.* Table 1). The supernatant clear liquid upon leaving undisturbed at a low temperature gave a further crop of crystals. Finally, a portion of the precipitate was recrystallized from a suitable solvent. All operations were performed under an atmosphere of purified nitrogen.

IR spectra were recorded using a Perkin–Elmer 225 grating spectrophotometer. KBr pressed discs or mulls in vaseline were employed for obtaining the spectra of the solid compound.

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