CHEMISTRY LETTERS, pp. 163-164, 1972. Published by the Chemical Society of Japan

SYNTHESES OF COPPER(I) TRIPHENYLPHOSPHINE COMPLEXES

Toshiyuki SHONO, Yoshihiko FUJII and Koichiro SHINRA
Department of Applied Chemistry, Faculty of Engineering, Osaka University
Yamada-Kami, Suita, Japan 565

Bis(triphenylphosphine)acetylacetonato copper(I) and analogous seven copper(I)triphenylphosphine chelates were prepared from various cupric complexes by reducing directly with triphenylphosphine

Copper(II) salts are known to be reduced by tertiary phosphine$^{1)}$, but the literature contains no reference to the direct synthesis of copper(I) complexes by the reaction of copper(II) complexes and tertiary phosphine.

Thus, addition of sodium boronhydride to the colorless solution obtained by mixing copper(II) sulfate and triphenylphosphine(PPh_3) in ethanol yields $[Cu(BH_4)(PPh_3)_2]$. Treatment of $[Cu(BH_4)(PPh_3)_2]$ with sodium acetylacetonate$^{2)}$affords $Cu(I)(acac)(PPh_3)_2$. In 1969 Nast and Lepel reported$^{3)}$that $Cu(I)(acac)(PPh_3)_2$ was obtained by mixing $Cu(I)(acac)2.5NH_3$ with an ether solution of triphenylphosphine in liquid ammonia. Recently the same complex was prepared from triphenylphosphine copper(I)chloride with thallium(I) acetylacetonate in benzene$^{4)}$. The syntheses of the trialkylphosphine complexes of various copper(I) N,N-dialkyldithiocarbamates are described by Kowala$^{5)}$. All of the above mentioned methods started from the copper(I) complexes.

We now report new and simple procedures to prepare analogous Cu(I) chelates from Cu(II) complexes. Di-μ-methoxobis(acetylacetonato)dicopper(II), $[Cu(acac)(CH_3O)]_2$$^{6)}$, was stired in molten PPh_3 at 90°C for 2hrs in a nitrogen atmosphere. The obtained solid mass extracted with ether to remove excess PPh_3. The residue was recrystallized from cyclohexane to give colorless plates corresponding to the formula $Cu(acac)(PPh_3)_2$. The yield was quantitative. I.R.(nujol mull): 1479, 1434, 1095, 1028, 742, 698, 512, 502 and 494cm^{-1} for PPh_3 1597, 1510, 1249, 915, 771, 688, 648 and 619cm^{-1} for acetylacetonate group and 440cm^{-1} for the (Cu-O) stretching vibration. Bis(acetylacetonato)copper(II) was treated in molten PPh_3 at 150°C for 2hrs in a nitrogen atmosphere. The solid mass was treated in a same manner as above. Colorless plates were obtained in a 80% yield.

Salicylaldehydato·copper(I) was prepared from di-μ-methoxobis(salicylaldehydato)-dicopper(II)$^{7)}$ or from bis(salicylaldehydato)copper(II). This complex was recrystallized from ethanol to give light yellow pyramidal crystals corresponding to the formula $Cu(Sal)(PPh_3)_2$. The yield was 70%. I.R.(nujol mull): 1497, 1435, 1098, 1028, 748, 695, 513, 503 and 490cm^{-1} for PPh_3 1620, 1141, 1022, 899 and 731cm^{-1} for the salicylaldehyde group and 425cm^{-1} for the (Cu-O) stretching vibration. The above mentioned reactions probably proceed by a radical mechanism. Support for this assumption is derived from the fact that the methylmethacrylate monomer polymerizes easily in these reaction systems. Details concerning this polymerization reaction will be reported separately.$^{8)}$

$$Cu(II)L_2 + 2PPh_3 \longrightarrow Cu(I)L(PPh_3)_2 + L\cdot$$

In addition to the acetylacetone(A) and salicylaldehyde(B), 5-nitro-salicylaldehyde(C), 2-hydroxy-1-naphthoaldehyde(D), 2-hydroxy-acetophenone(E), 3-formylcamphor(F), trifluoro-acetylacetone(G) and diethyl-dithiocarbamate(H) were used as ligand (L). In each case corresponding $Cu(I)L(PPh_3)_2$ was obtained easily. Melting points,recrystallization solvents and NMR data of the $Cu(I)L(PPh_3)_2$ are shown in Table 1. Elementary analyses of eight copper(I) chelates are shown in Table 2. The results of the elementary analyses are in good agreement with the calculated values for the $Cu(L)(PPh_3)_2$. All of these compounds were diamagnetic(magnetic susceptibilities were measured using a Gouy balance at room temperature).

The crystal structure of $CuX(PPh_3)_2$ compounds where X is β-diketone mono anion were recently determined$^{9)}$. A feature common to these complexes were surprisingly large P-Cu-P angles$^{10)}$.

Table 1 Melting points,recrystallization solvents and NMR data of Cu(I) complexes

Ligand	Recrystallization solvent	M.p.(°C)	NMR(τ) (in $CDCl_3$)
A	Cyclohexane	177-179	2.75(30H,S),4.92(1H,S),8.22(6H,S)
B	Ethanol(with PPh_3)	175	2.33(1H,S),2.80(34H,S)
C	Acetonitrile	214-215	2.00(1H,S),2.79(33H,S)
D	Toluene	194-196	-0.10(1H,S),2.82(34H,S),3.26(2H,D)
E	Methanol	153-155	2.80(34H,S),7.66(3H,S)
F	Acetonitrile	105-107	1.98(1H,S),2.82(30H,S),7.70(1H,S) 8.05(4H,S),9.21(6H,D),9.29(3H,S)
G	"	154-155	2.80(30H,S),4.70(1H,S),8.18(3H,S)
H	"	144-146	2.80(30H,S),6.21(4Q,Q),8.80(6H,T)

Table 2 Elementary analyses of copper(I) chelates

Ligand	Found(%)					Calcd. for $Cu\cdot(L)(PPh_3)_2$ (%)				
	C	H	N	S	Cu	C	H	N	S	Cu
A	71.90	5.30			9.26	71.66	5.43			9.24
B	72.87	4.95			9.14	72.82	4.98			8.97
C	68.50	4.49	1.85		8.62	68.48	4.54	1.86		8.43
D	74.22	4.88			8.57	74.35	4.91			8.37
E	73.12	5.21			9.01	73.07	5.16			8.79
F	73.34	6.08			8.31	73.57	5.91			8.21
G	66.20	4.57			8.73	66.44	4.62			8.57
H	66.85	5.73	1.84	8.75	8.49	66.87	5.48	1.90	8.71	8.63

References

1) W.E.Hatfield and R.Whyman Transition Metal Chemistry Vol.5 Marcel Dekker,(1969)
2) F.Cariati and L.Naldini J.Inorg.Nucl.Chem.,28 2243 (1966)
3) R.Nast and W.Lepel Chem.Ber.,102 3224 (1969)
4) D.Gibson J.Chem.Soc.,(A),367 (1970)
5) C.Kowala and J.M.Swan Aust.J.Chem.,19 555 (1966)
6) J.A.Bertrand and R.I.Kaplan Inorg.Chem.,4 1657 (1965)
7) T.Inazu Bull.Chem.Soc.Japan 42 2291 (1969)
8) T.Shono, Y.Yamashoji and K.Shinra Bull.Chem.Soc.Japan in contribution.
9) M.Bartlett and G.J.Polenik Acta Crystallogr., A25 S173 (1969)
10) S.J.Lippard and G.J.Polenik Inorg.Chem.,10 1323 (1971)

(Received December 8, 1971)