Journal of Organometallic Chemistry
Elsevier Publishing Company Amsterdam
Printed in The Netherlands

PHENYLCOPPER COMPLEXES WITH TERTIARY PHOSPHINES AND WITH TRIPHENYLBORANE

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(Received August 8th, 1966)

In a previous paper[1] the reactions involving a formation of phenylcopper (CuPh) were described, and pure CuPh as well as some complexes with LiPh and $Mg(Ph)_2$ were reported. The present work deals with CuPh complexes with PPh_3, PBu_3 and BPh_3 and was undertaken with the aim of studying the possibility of stabilization and/or solubilization of organocopper compounds by complex formation.

Attempts to isolate complexes with $AlPh_3$, NPh_3, $AsPh_3$, $SbPh_3$ and $BiPh_3$ were unsuccessful.

RESULTS

Reactions of phenylcopper with triphenylphosphine and tributylphosphine

PPh_3 reacts with solid CuPh suspended in tetrahydrofurane, toluene, benzene or diethyl ether to give yellow soluble products. With $CuPh/PPh_3$ ratios of 0.33–3, the crude crystalline product is a mixture of different complexes. Its composition was found to vary from $(CuPh)_{1.8}PPh_3$ to $(CuPh)_{3,3}Ph_3$. With a $CuPh/PPh_3$ ratio of 5, unreacted CuPh is recovered, while the ratio in the solution approaches 3.

Under appropriate conditions, by a single crystallization from toluene almost pure crystalline complexes $(CuPh)_2PPh_3$ and $(CuPh)_3PPh_3$ were obtained. Repeated crystallizations lead to compounds with higher copper content and deeper colour.

Only partially phenylated derivatives were obtained from $CuBrPPh_3$ by reaction with LiPh, while $CuBr(PPh_3)_3$ failed to react.

Using PBu_3 as complexing agent in ethyl ether or toluene, with Cu/PPh_3 ratios from 0.33 to 1, no crystallizable products are obtained, owing to the high solubility. With an excess of CuPh in n-pentane, a crystalline solid can be separated. The $CuPh/PPh_3$ ratio in the solution approaches 2, and the CuPh excess is recovered almost pure as insoluble residue.

All the above complexes are diamagnetic and monomers in toluene at concentrations from 1 to 3% w/w. The crystalline products are stable for weeks under nitrogen at room temperature.

Hydrolysis of the phenyl groups bonded to copper occurs easily in moist solvents. In n-heptane at 0° a Cu/Ph ratio 1 is found, while at higher temperature some biphenyl is formed, as in the case of CuPh. The ligand is recovered after hydrolysis mainly as such or as phosphine oxide: the latter is the main product in the presence of air.

Reaction of phenylcopper with triphenylborane

An equivalent amount or excess of BPh_3 in diethyl ether reacts with CuPh to give a grayish microcrystalline powder consistent with the formula $CuBPh_4$. The product decomposes slowly in the air. It is easily hydrolyzed by moist organic solvents even at 0°, giving mainly benzene, in an amount accounting for the phenyl groups of both BPh_3 and CuPh. $CuBPh_4$ is very soluble in pyridine, from which the yellowish complex $CuBPh_4 \cdot 4$ Py is precipitated by water.

TABLE 1

INFRARED SPECTRA OF TRIPHENYLPHOSPHINE COMPLEXES[a]

Assignments (*Ref.* 3)	C_6H_5Br (*Ref.* 3)	PPh_3	*CuPh* (*Ref.* 1)	$(CuPh)_2PPh_3$	$CuBrPPh_3$ (*Ref.* 2)
ω_{17}	1637				
ω_4	1580	1583 m	1585 vw	1584 ms	1582 m
ω_{18}	1580			1562 sh	1577 sh
		1480 vs		1476 vs	1482 s
ω_5	1477				
			1470 s	1470 m	
		1435 vs		1434 vs	1435 vs
ω_{19}	1443				
			1417 vs	1417 ms	
	1379	sh	1384 sh	1384 sh	1380 sh
	1351	sh			
	1320	1326 w	1330 w	1320 sh	1330 w
ω_{20}	1299	1308 m	1300 s	1300	1308 m
		1283 mw	sh		1283 w
	1266	1272 mw	sh	1274 s	
ω_7		1181 m	1189 m	1186 sh	1184
	1174				
ω_{21}	1159	1159 m	1162 m	1162 m	1160
ω_{22} and		1090 vs		1095 s	1096 vs
ω_6 (ω_x)	1068	1070 s		1072 w	1070 s
			1057 s		
			1045 s	1047 w	
ω_8	1019	1026 s		1025 m	1030 ms
			1017 s	1009 sh	
ω_9	999	997	990 s	998 m	998 m
ω_{25}	987			989 sh	
ω_{12}	962				
		917 mw		922 w	917
ω_{26}	903				
		910 mw	909 m	909 w	910
ω_{13}	831	851 ms	861 m	845 m	850 m
		753			754
ω_{27}	735	747 vs		746 broad vs	745 vs
		743			
			723	721	
ω_{28} and	683	692	696	693	694
ω_{10} (ω_x)	675	698	672	705	707

[a] Frequencies in cm^{-1}; v = very; s = strong; m = medium; w = weak; sh = shoulder.

TABLE 2

INFRARED SPECTRA OF TRIPHENYLBORON COMPOUNDS[a]

Assignments	*$AgBPh_4$*	*$CuBPh_4$*	*$TlBPh_4$*	*$NaBPh_4$*	*NH_4BPh_4*	*BPh_3*
		1600				
ω_4	1575 ms	1575 ms	1580 ms	1580 ms	1580 ms	1587 vs
ω_{18}	1564 sh			1557 sh		1564 sh
ω_5	1478 vs	1476 vs	1478 vs	1478 vs	1480 vs	
ω_{19}	1424 s	1427 s	1425 s	1430 s	1430 s	1434 vs
		1348 mw		1393 vs	1393 vs	1350 ms
ω_6 (ω_x) and ω_{20}	1315 m	1313 mw	1310 mw	1311 mw	1310 mw	1314 s
	1270 sh	1272 s	1273 m	1260 s	1270 s	1283 vs
	1262 s	1260 sh				1263 sh
						1240 vs
ω_7	1180	1180 m	1187 vs	1190 ms	1189 vs	1192 w
ω_{21}	1158 ms	1159 ms				
	1142 s	1142 s	1159 vs	1156 s	1157 vs	
	1128 sh	1130 sh	1133 w	1131 w	1123 w	1131 w
ω_{22}	1065 ms	1065 ms	1069 m	1070 m	1070 m	1074 m
ω_8	1028 ms	1030 ms	1028 s	1031 ms	1026 s	1027 ms
ω_9	996 m	995 m	996 mw	994 m	996 m	998 ms
						990 sh
ω_{25}	978 m	974 m	989 mw	979 w	992 m	979 m
	921 s	917 ms	917 ms	923 w	919 s	938 ms
	863 ms	866 ms	866 ms	869 m	865 m	898 ms
	850 ms	849 ms	852 vs	853 vs	852 vs	884 vs
ω_{10} (ω_x)						775 s
ω_{27}	743 vs	739 vs	747 vs	747 vs	747 vs	745 vs
			739 vs	739 sh	739 vs	
	732 vs	729 vs				
ω_{10} (ω_x) and ω_{28}	715 vs	715 vs	713 707 vs	723 vs	715 710 vs	689 vs,vb

[a] Frequencies in cm^{-1}; v = very; s = strong; m = medium; w = weak; sh = shoulder, br = broad.

Infrared spectra

Apart from some intensity variations and small shifts of a few phenyl absorption bands, the IR spectra of $(CuPh)_2PPh_3$ and $(CuPh)_3PPh_3$ are very close to the superimposed spectra of CuPh and PPh_3 in the region examined. The absorption frequencies of PPh_3 in the complexes are almost exactly as in $CuBrPPh_3$.

The spectrum of $CuBPh_4$, on the contrary, is markedly different from that of BPh_3, mainly in the 1390–1100 and 680–800 cm^{-1} regions, where substituent sensitive frequencies ω_6 and ω_{10} are found. In the same regions the spectrum of $CuBPh_4$ and $AgBPh_4$ can be distinguished from that of the other tetraphenylboron compounds, showing a higher number of bands in the 1270–1120 cm^{-1} region and a different pattern for the splitting of the ω_{27} and ω_{28} bands (750–715 cm^{-1}).

The IR spectra, frequencies of adsorption bands and assignments of starting compounds and related complexes are listed in the Fig. 1, 2 and Tables 1, 2.

The bands about 1095 and 1070 cm^{-1} in the $(CuPh)_nPPh_3$ and $CuBrPPh_3$ complexes can be assigned to the in-plane C–H bending and to the substituent sensitive $\omega_6(\omega_x)$ mode of the PPh_3 ligand. The displacement towards higher frequencies as compared with free PPh_3 is in agreement with the findings of Deacon and Green[4] on complexes of the type $(PPh_3)_2MgX_2$ (M = Zn, Cd, Hg; X = Cl, Br, I). A similar displacement is observed also for the second ω_x mode (ω_{10}).

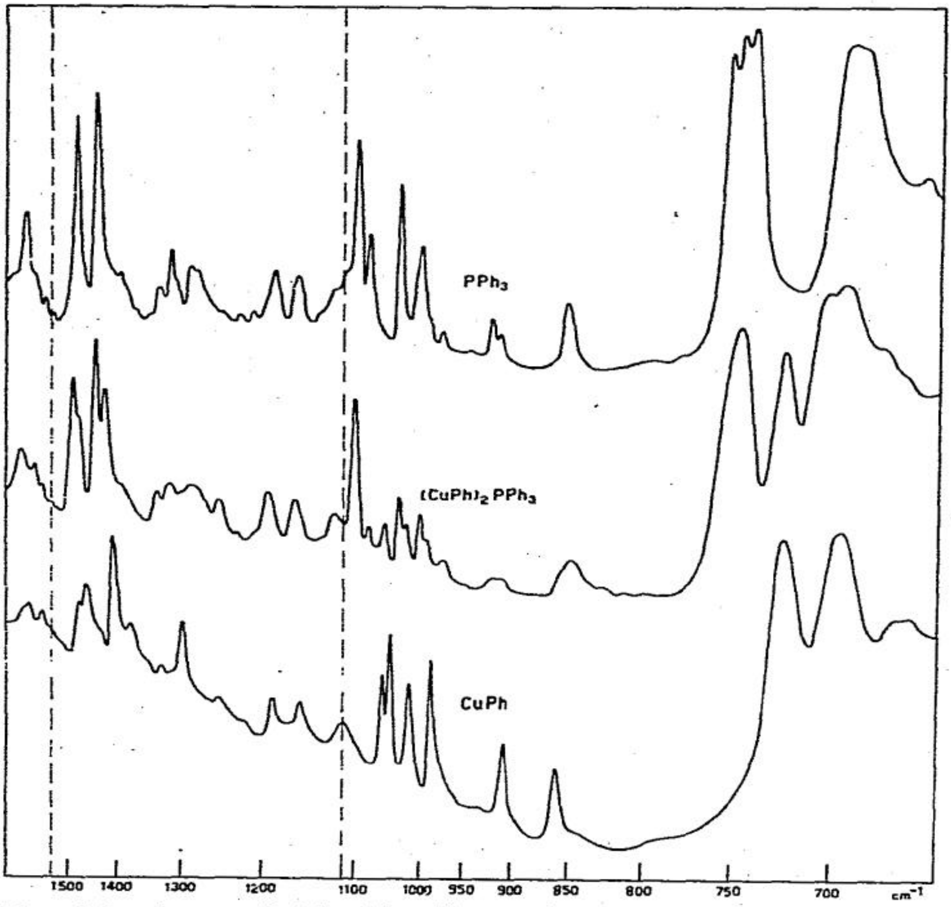

Fig. 1. Infrared spectra of triphenylphosphine complexes.

In BPh_3, either the 1283 and/or 1240 cm^{-1} band could be assigned to the $\omega_6(\omega_x)$ mode. In compounds containing the residue Ph_2B, only one strong absorption was found[5,6] between 1280 and 1250 cm^{-1} while in the $PhBF_2$ it is found[7] at 1292 cm^{-1}. In $CuBPh_4$ and $MBPh_4$ (M = Na^+, Tl^+, NH_4^+), the corresponding assignment can be confidently made for the band at 1273–1260 cm^{-1}.

The very strong absorptions in the range 723–745 cm^{-1} are safely assigned in all examined compounds to the out-of-plane C–H deformation γ(C–H) (ω_{27}). In CuPh (723 cm^{-1}) and BPh_3 (745 cm^{-1}), the frequency is some 10 cm^{-1} lower than expected from the linear plot frequency-reduced mass given by Margoshes and Fassel[8].

DISCUSSION

Phenylcopper/tertiary phosphine complexes

The results of the present work, showing that only PPh_3 out of the triphenyl derivatives of group VB elements forms isolable complexes with PhCu, are in keeping with the relative coordinating affinities ($N < P > As > Sb > Bi$) of group VB ligand atoms towards alkynylcopper and organogold compounds[9-12].

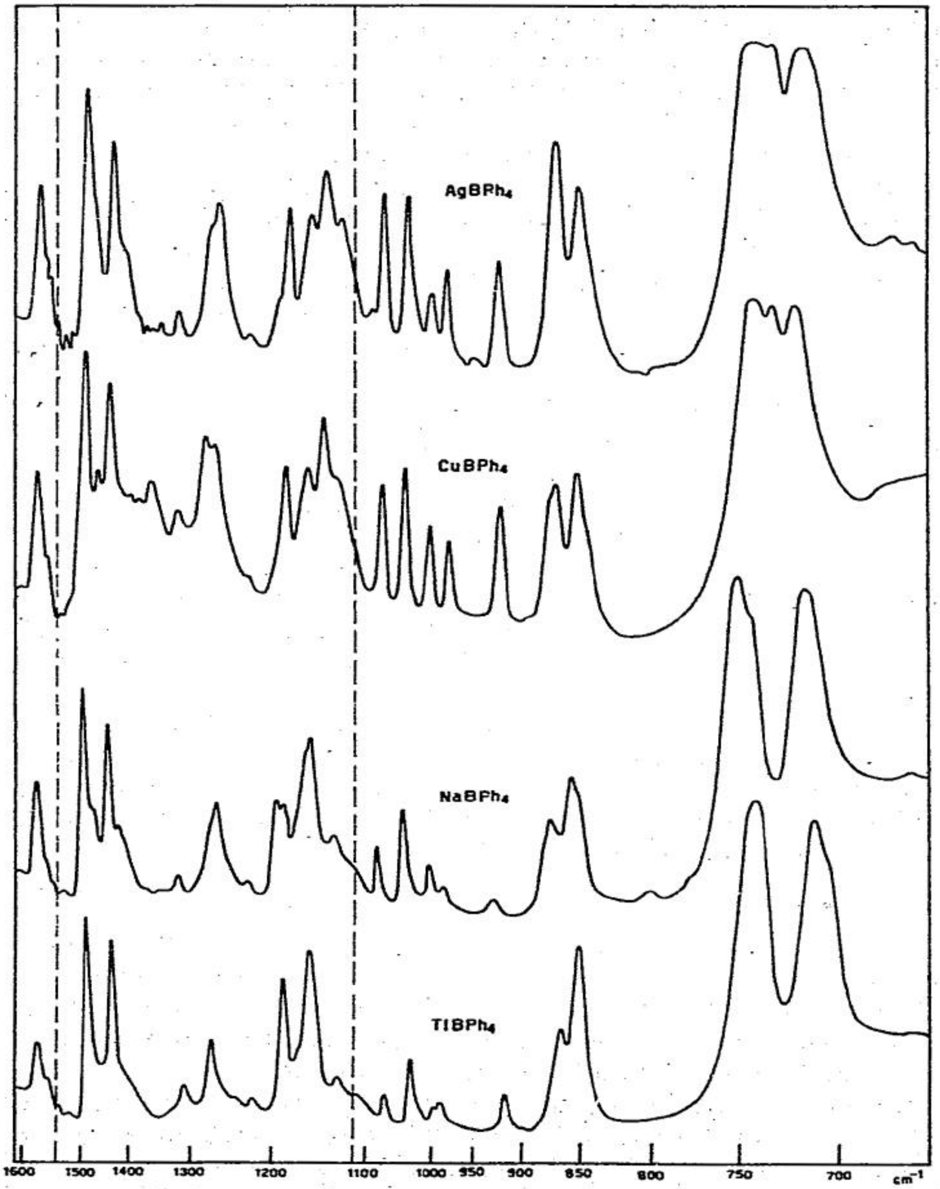

Fig. 2. Infrared spectra of tetraphenylboron compounds.

The fact that PhCu can be moderately stabilized and markedly solubilized by complex formation with PPh_3 or PBu_3 is in contrast with the behaviour of methylcopper, which forms a highly unstable complex with PPh_3[2]. On the other hand these complexes are easily hydrolyzed and oxidized; in contrast to $AuPhPPh_3$[11].

As for the stoicheiometry, the tendency to coordinate more than one CuPh to one PPh_3 is in contrast with the formulae of the $(CuX)_n(PPh_3)_m$ complexes ($n/m = 1, \frac{1}{3}, \frac{2}{3}$; X = Cl, Br, I)[13] and of the $CuCH_3(PPh_3)_3$ complex[2].

From the IR spectra, small interactions between the phosphine ligand and CuPh and minor effects on the Cu–C bond can be assumed to occur in the $(CuPh)_n \cdot PPh_3$ complexes.

Phenylcopper, insoluble in all solvents with which it does not react, can be possibly regarded as a coordination polymer (on the basis of interaction of filled metal *d* orbitals with antibonding π orbitals of the phenyl group)[14]. Tertiary phosphines should reduce the polymer to lower aggregates by competition with phenyl groups as ligands. A similar view was formerly proposed for the ethynylcopper compounds, which are also thought to be coordination polymers[10].

Tetraphenylboroncopper

An impure sample of Cu^IBPh_4 was previously prepared by a very slow reaction between $CuBr_2$ and $LiBPh_4$[15]. Better results were reported by careful acidification of $CuBPh_4 \cdot 4\,Py$ obtained from the reaction of $KBPh_4$ with the copper derivative of acetoacetic ester in pyridine[16], but the $CuBPh_4$ we prepared by direct addition of CuPh to BPh_3 is better characterized and more stable.

The differences in the spectra of triphenylborane and tetraphenylboron derivatives clearly reflect a change in the phenyl groups arrangement around the boron atom. With the $MBPh_4$ complexes, the spectra of copper and silver compounds show differences which are greater than expected assuming the same structure as in the other salt-like compounds ("ate" complexes).

In accord with these results are the differences in reactivity between $LiBPh_4$ and $CuBPh_4$. The LiPh in the salt-like complex $LiBPh_4$ has no reactivity towards carbonyl compounds in the salt-like complex $LiBPh_4$, while $CuBPh_4$ still reacts with some carbonyl compounds[17]. Moreover, all the phenyl groups of $CuBPh_4$ are hydrolyzable, in contrast with those of $LiBPh_4$.

EXPERIMENTAL

General procedures, apparatus and reagents

Strictly anhydrous solvents were used. All the reactions and manipulations were carried out in an atmosphere of dry oxygen free nitrogen. Hydrolizable phenyl groups were determined as previously described[1]. Molecular weights were determined in toluene at 37° with a Mechrolab Vapor Pressure Osmometer Model 302. IR spectra were registered as KBr pellets with a Perkin Elmer 13 Spectrophotometer. Magnetic measurements were made by the Gouy method at room temperature.

CuPh was freshly prepared from CuBr and LiPh[1]. Commercial PPh_3 (purissimum Fluka) and PBu_3 (practicum Fluka) were used. BPh_3 was prepared from thermal decomposition of trimethylammonium tetraphenylborate[15]: commercial (practical) BPh_3 did not react satisfactorely with CuPh. $NaBPh_4$ (Kalignost) was purified by cristallization from acetone/benzene[18]. NH_4BPh_4, $TlBPh_4$ and $AgBPh_4$ were precipitated from Kalignost solution by the correspondent nitrates. The latter was prepared from methanolic solutions[15].

Phenylcopper/phosphine complexes

$(CuPh)_2PPh_3$. PPh_3 (1.53 g, 5.8 mmole) in toluene (30 ml) was added dropwise at 0° to a stirred suspension of CuPh (0.82 g, 5.8 mmole) in the same solvent (10 ml). A yellow-brown solution was slowly formed. After standing 1 h at room temperature the solution was filtered, concentrated to about 6 ml and cooled at −60° overnight. Some crystals were formed and then a good crystallization occurred at room temperature. The pale-yellow solid separated was filtered, washed with cold toluene and ether and thoroughly dried *in vacuo.* [Found: C, 66.22; H, 5.09; Cu, 23.90; P, 5.59; Ph, 28.00; Ph/Cu, 0.97; mol. wt. (3.3% w/w), 530. $C_{30}H_{25}CuP$ calcd.: C, 66.28; H, 4.64; Cu 23.39; P, 5.70; Ph, 28.37%; Ph/Cu 1.00; mol. wt., 544.]

$(CuPh)_3PPh_3$. PPh_3 (1.25 g, 4.8 mmole) in toluene (15 ml) was added dropwise at 0° to a stirred suspension of CuPh (1.90 g, 13.5 mmole) in the same solvent (10 ml), the mixture was allowed to warm to room temperature. After about 10 h stirring the solution was brown and the solid yellow. The solid was filtered, quickly washed with toluene and ether and thoroughly dried *in vacuo.* [Found: C, 63.41; H, 4.95; Cu, 28.08; P, 4.42; Ph, 35.13; Ph/Cu, 1.03; mol. wt. (1.23% w/w), 673. $C_{36}H_{30}CuP$ calcd.: C, 63.19; H, 4.42; Cu, 27.86; P, 4.53; Ph, 33.80%; Ph/Cu 1.00; mol. wt., 684.]

$(CuPh)_2PBu_3$. A solution of Bu_3P (0.9 ml, 3.6 mmole) in diethyl ether (20 ml) was added dropwise at 0° to a stirred suspension of CuPh (1.90 g, 13.5 mmole) in the same solvent (15 ml). The solution became immediately deep yellow, then slowly orange-brown. After 5 h stirring the solid still present was filtered off and washed. CuPh (0.65 g, identified by IR spectrum) was recovered. The solution evaporated left a viscous yellow brown residue, soluble in aliphatic and aromatic hydrocarbons. In the presence of air it slowly decomposes to black.

When the above reaction was conducted in n-pentane, we were able to isolate from the orange solution, by concentration and cooling, a brilliant yellow crystalline compound. In the presence of air it immediately becomes red, and in a few seconds it is transformed in a brown oil. [Found: C, 55.28; H, 7.60; Cu, 27.65; P, 5.94; Ph, 32.32; Ph/Cu, 0.96; mol. wt., (three different runs 2.2–3.6 w/w), 479–521. $C_{24}H_{37}PCu$ calcd.: C, 59.60; H, 7.71; Cu 26.29; P, 6.40; Ph, 31.88%; Ph/Cu, 1.00; mol. wt., 484.]

The high Cu and the low P contents are probably due to the presence of some $(CuPh)_3 \cdot PBu_3$. Analytical results for C and H are low owing to decomposition in the sampling of the product.

$CuBPh_4$. A clear solution of BPh_3 (1 g, 4.5 mmole) in diethyl ether (40 ml) was added dropwise at 0° to a stirred suspension of CuPh (0.58 g, 4.1 mmole) in the same solvent (15 ml), and the mixture was allowed to warm to room temperature*. Stirring was prolonged for about 10 h, then the white voluminous product was filtered and washed with ether until the excess of BPh_3 was eliminated. The whitish microcrystalline product powder was dried *in vacuo*; 1.2 g, 75% yield; m.p. 110° darkening 135–137° dec. (Found: C, 75.80; H, 5.55; B, 2.85; Cu, 16.20. $C_{24}H_{20}BCu$ calcd.: C, 75.30; H, 5.27; B, 2.83; Cu, 16.60%.)

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* At 0° no reaction was observed even after many days.

$CuBPh_4 \cdot 4$ Py. The above compound was dissolved in pyridine and the yellow-brown solution was precipitated by water, washed with water and dried *in vacuo*. (Found: C, 74.95; H, 6.18; B, 1.80; Cu, 9.47; N, 7.73. $C_{44}BCuN_4$ calcd.: C, 75.58; H, 5.77; B, 1.55; Cu, 9.09; N, 8.01%.) IR spectrum was identical with a product obtained according to Nesmeyanov and Coll[16].

ACKNOWLEDGEMENT

We thank the NATO and the Italian National Research Council (C.N.R.) which in part supported this work. To the Microanalytical Laboratory of T.H. of Munich we are indebted for some analyses.

SUMMARY

Reactions of phenylcopper with some representative Lewis bases and acids are described. The complexes $(CuPh)_2PPh_3$, $(CuPh)_3PPh_3$, $(CuPh)_2PBu_3$ are reported. The IR absorption frequencies of the PPh_3 complexes in the 1600–700 cm^{-1} region are assigned and discussed. Tetraphenylboroncopper is obtained by addition of CuPh to BPh_3. The IR spectrum is assigned and compared with those of other tetraphenylborate compounds.

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