Journal of Organometallic Chemistry, 81 (1974) 87—95

REACTIONS OF ARYLCOPPER COMPOUNDS WITH ACTIVE HYDROGEN COMPOUNDS

NEW STABLE ORGANOCOPPER DERIVATIVES OF THE ALIPHATIC SERIES

N MARSICH and A. CAMUS

Institute of Chemistry and CNR Center, University of Trieste, 34127 Trieste (Italy)

(Received March 26th, 1974, in revised form May 31st, 1974)

Summary

Some new stable organocopper derivatives of the aliphatic series were prepared by reaction of aryl copper compounds with bis(diphenylphosphinosulphide)methane or malononitrile. A new kind of synthesis for Cu^IBL_2 complexes [B = conjugated base of acetylacetone, ethyl acetoacetate, diethyl malonate, ethyl cyanoacetate, L = triphenylphosphine, L—L = bis(diphenylphosphino)methane or 1,2-bis(diphenylphosphino)ethane] starting from organocopper derivatives is also reported.

Alkylcopper compounds are usually unstable [1]. Recently, however, we isolated a copper derivative of bis(diphenylphosphino)methane (dpm), which, though containing the metal σ-bonded to sp^3 carbon atoms, was stable at room temperature in an inert atmosphere and moderately stable also in air [2].

Apart from the perfluoroderivatives [3], there are only a few other fairly stable organocopper compounds with the metal atom bonded to an aliphatic carbon (some α-cuprio-benzylideneamines [4], tetrakis(trimethylsilymethylcopper (I))[5] and a trimethylmethylenephosphorane derivative [6]). As the dpm derivative was produced by reaction between arylcopper compounds and dpm by a quantitative exchange reaction of the metal with an active hydrogen of the methylene group of the ligand, we tried to extend this kind of reaction to other active hydrogen compounds.

Results and discussion

Among the numerous compounds that were treated with organocopper derivatives only bis(diphenylphosphinosulphide)methane ($dpms_2$) and malononitrile (mn) gave isolable stable products. Both derivatives have considerable thermal stability and can be kept unchanged for months in an inert atmosphere and for many hours in air. The reactions occur with quantitative formation of the arene corresponding to the organometallic compound, following eqn. 1.

$$(\mathrm{ARCu})_n + n\,\mathrm{HB} \rightarrow n\,\mathrm{ArH} + (\mathrm{CuB})_n \qquad (1)$$

(B = conjugated base of the active hydrogen compound)

(A) Reaction of ArCu with dpms$_2$

The reaction between phenyl- or tolyl-copper and dpms$_2$ in toluene gives an ivory diamagnetic powder of formula Cu(dpms$_2$—H)·1/2 toluene (I). The solvent cannot be completely removed in high vacuum. I is markedly soluble in common solvents, except ether and ligroin, but evidently reacts with many of them, such as chlorinated solvents or carbon disulphide. Hydrolysis with aqueous hydrochloric acid gives a product of formula CuCl·dpms$_2$, approximately dimeric in dichloroethane (DCE).

On the basis of molecular weight, I is tetrameric in toluene, from which it can be recrystallized unchanged. Since the coordinating position of the phosphine is blocked by sulphur, the polymerization is probably due to the latter element. Coordination between sulphur and copper is very common and recently structures of copper complexes with trimethylphosphine sulphide have been reported [7].

The IR spectrum of I is completely different from that of the ligand (Fig. 1). In particular, the region of phenyl absorption is highly simplified,

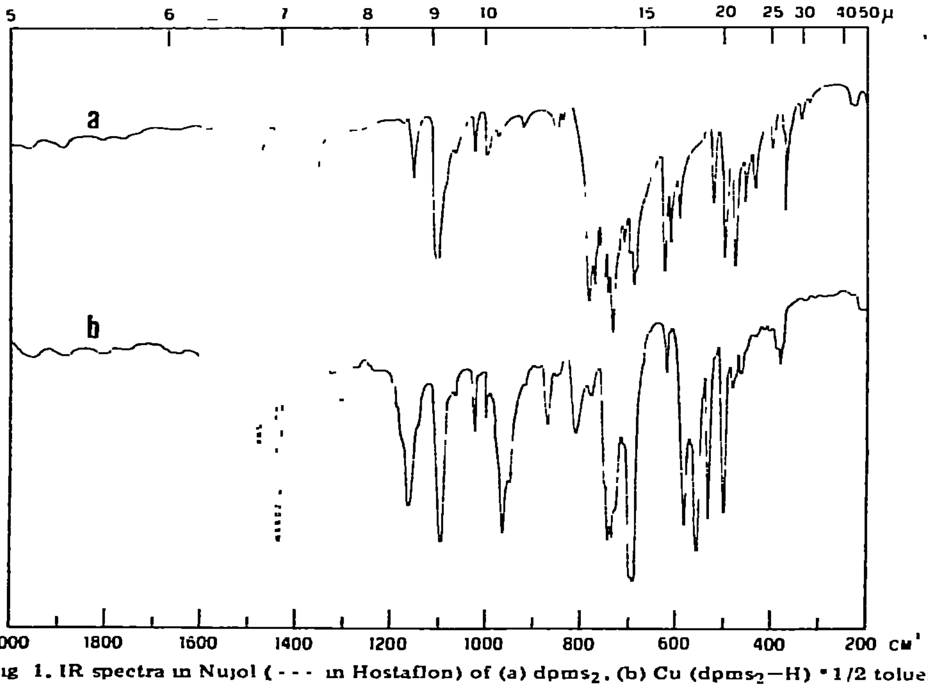

Fig 1. IR spectra in Nujol (- - - in Hostaflon) of (a) dpms$_2$. (b) Cu (dpms$_2$—H) · 1/2 toluene.

while the bands of P = S stretching, near 600 cm^{-1}, are shifted towards lower frequencies, in agreement with the expected behaviour of a P = S group bonded directly to the metal [8].

(B) Reaction of ArCu with mn

The reaction between phenyl- or tolyl-copper and mn in toluene gives a compound of approximate formula $[Cu(mn{-}H)]_n$ (II), which always contains low percentages of the reaction solvent. II is assumed to be polymeric on the basis of its high thermal stability and its low solubility in most organic solvents In pyridine, however, the compound dissolves easily. From the orange solution ether precipitates a light brown powder of composition $[Cu(mn{-}H)]_2py_3$, scarcely stable at room temperature even in an inert atmosphere.

The IR spectrum of II shows clearly that the reaction occurred on the methylene group, as all the bands assigned to this group in the free ligand [9] have disappeared (Fig. 2). The CN group is also involved in the bond, probably as bidentate nitrile-π-system, because its stretching occurs at reduced frequencies [10]. Bands around the free nitrile frequency are absent. Considerable spectral simplification occurs upon formation of the complex with respect to both the free ligand and its bromo derivative, which we used as a model for comparison.

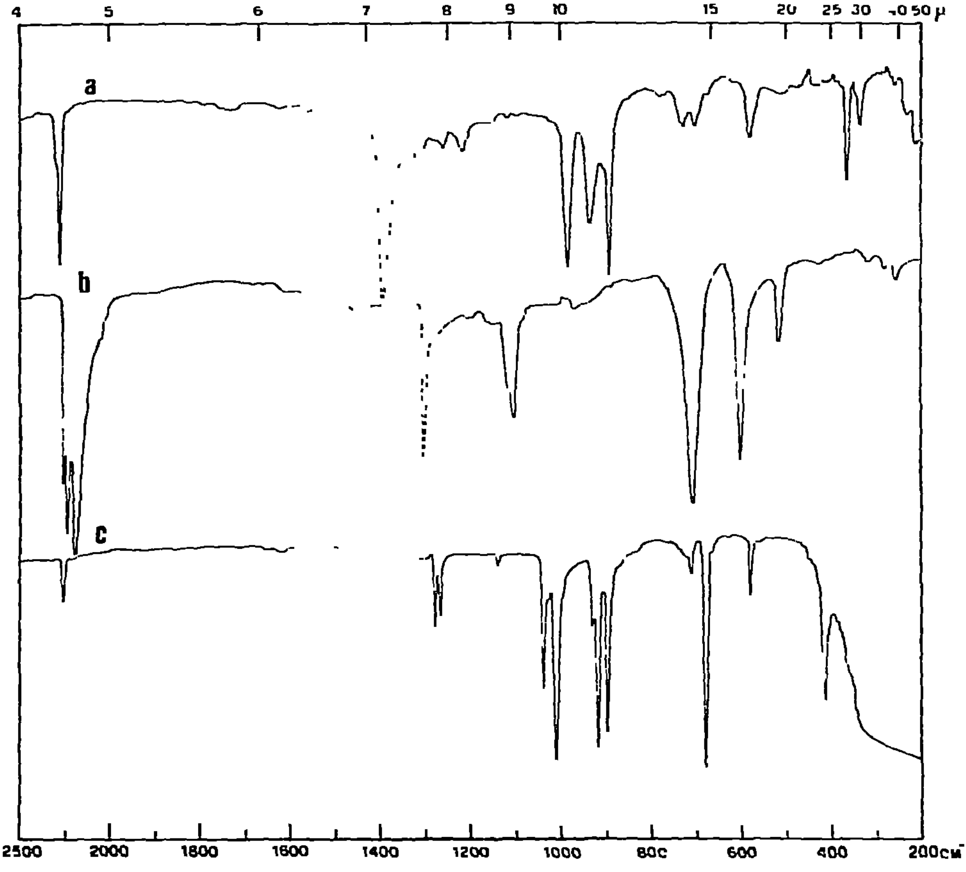

Fig. 2. IR spectra in Nujol (- - - in Hostaflon) of (a) mn, $[Cu(mn{-}H)]_n$, (c) CNCHBrCN (KBr plates).

The CN absorption region, however, besides a marked increase in extinction coefficient, shows several splittings, as in the case of copper derivatives of tricyanomethan [11]. Furthermore, bands in the spectrum of the complex are broad, as if they were envelopes of bands very near in absorption. In the possible region of Cu—C stretching absorption only three bands are present (708vs, 600s, 515w cm^{-1}). However, there are very few data available in literature, and those there are concerning a variety of compounds and conditions [6, 12, 13], do not permit the assignment of the frequency of the metal—carbon bond. We are now trying to get some theoretical information on this point.

The IR spectrum of the complex with pyridine shows a CN-stretching band at an even higher frequency than the free ligand, which could be evidence of linear CuNC bonds [14]. As for the Cu—C stretching, there are two new bands at 534s and 447m cm^{-1}, which are tentatively assigned to this mode.

II is scarely reactive towards the usual small molecules. Unlike the copper complex of dpm, it does not react with carbon disulphide, sulphur dioxide or alkyl halides. Acetyl chloride reacts in part, but the carbonyl group is not introduced into the molecule. With HCl, II undergoes hydrolysis, followed by the formation of the chlorinated complex CuCl·mm, identical with the reaction product from copper chloride and mn [15]. As expected, the IR spectrum of this complex again shows the fundamental structure of mn.

II reacts with triphenylphosphine to give a white stable complex, of stoichiometry Cu(mn—H)(PPh$_3$)$_2$, which can also be obtained from the organometallic derivative by the simultaneous addition of mn and triphenylphosphine in the appropriate ratio. The IR spectrum of this compound keeps the characteristics of the starting compound II in the CN region (with an even large shift to lower frequencies), while at 600^{-1} the bands are mainly those of the phosphine. The 600 cm^{-1} band of II disappears, probably shifted to the 540-480 cm^{-1} region, which is very complex.

Attempts to obtain substituted dinitriles by reaction of Cu(mn—H) (PPh$_3$)$_2$ with alkyl halides were unsuccessful.

(C) Reaction of ArCu with active hydrogen compounds to give intermediate reactive species

Some other active hydrogen compounds, namely acetylacetone (acac), ethyl acetoacetate (eaa), diethyl malonate (dem), ethyl cyanoacetate (eca)[*] reacted with arylcopper compounds, but gave derivatives unstable in the experimental conditions. These unstable moieties could be fixed with mono or bidentate tertiary phosphines, to give Cu^{I}BL$_2$ complexes (eqn. 2).

$$\mathrm{CuR + BH + 2L \rightarrow CuBL_2 + RH} \qquad (2)^{**}$$

---

[*] Phenyl acetonitrile, *N,N*-dimethylbenzylamine, chloromethylsulfone and bis(diphenylarsinosulphide)-methane did not react We could not isolate definite compounds from the reaction with bis(diphenylphosphinoxide)methane

[**] The polymeric nature of the compounds is not taken into account. In benzene the triphenylphosphino derivatives are monomeric, the dpm complexes dimeric.

[B = conjugated base of acac, eaa, dem; L = 1 equivalent of triphenylphosphine, dpm or 1,2-bis(diphenylphosphino)ethane(dpe)].

The above reaction, which occurs rapidly and with high yields (50-95%), offers a convenient alternative to the methods previously reported for the synthesis of some acac complexes of this kind [16]. The new complexes obtained (Table 1) are white diamagnetic compounds, stable in air in solid dry state, but easily oxidizable in solution. On the basis of their infrared characteristic patterns in the 1700-1500 cm^{-1} region (two strong absorption bands at about 1600 and 1500 cm^{-1}, due to the coupled C=O and C=C stretching modes) acac, eaa and dem are assumed to react in the enolic form, as in the known case of Cu(acac—H) $(PPh_3)_2$ [16c], but Cu(eca—H) $(PPh_3)_2$ could be a true organometallic compound. In its infrared spectrum the band at about 1500 cm^{-1} is absent and the C=O stretching mode occurs at higher frequencies, in the range of those reported for $R_2C{=}C(Cu)COOR$ compounds [17] or for the Pt—acetylacetone complexes, in which the β-diketone is bonded via the γ-carbon atom [18].

The Cu^{I}eca complexes with dpm and dpe also differ markedly from those of the other series.

The dpe derivative could be isolated only as Cu^{I}(eca—H)$_2$(dpe)$_3$. The solid complex exists in two modifications, which differ in their solubility properties and in their solid state infrared spectra, although neither contain solvent of crystallization. In DCE the eca is slowly displaced to give the known $(CuCl)_2(dpe)_3 \cdot 2DCE$ [19].

The reaction product from ArCu, eca and dpm in ether seems to be an impure $CuBL_2$ complex, but by repeated crystallization from benzene its composition moves gradually to Cu/dpm/eca = 3/3/2. This unexpected stoichiometry is supported by the isolation of the same solid by the reaction between [Cu(dpm—H)]$_3$ and eca, but we cannot at present exclude the presence of a mixture, because the infrared spectrum shows a clear splitting of the CN-stretching in a doublet and the characteristics of the product are not perfectly reproducible in different preparations. In DCE the eca is slowly displaced, giving as main compound CuCl·dpm [19].

On the whole the reactivity between organocopper species and active hydrogen compounds confirms the indication obtained from the structure of the [Cu(dpm—H)]$_3$ derivative [2], i.e. that hydrogen activity is important for its exchange reaction with copper, but that the stabilization of the organometallic compound requires the presence in the molecule of other atoms coordinated to the metal. Similar results have already been found with organocopper compounds of the aromatic series [20].

Experimental

General

Arylcopper compounds were prepared and isolated as previously described [21]. dpms$_2$ was prepared following the method of Issleib and Baldauf [22]. Other reagents were industrial products, distilled before use. The mn was purified by sublimation. Reactions were carried out under nitrogen at 0°C in dry solvents.

TABLE 1

ANALYTICAL DATA

Compound [a]	Recrystallized from	m p	analysis (%) found (calcd) Cu	C	H	N	ν(CN)	IR (cm^{-1}) 1700 - 1500 region [b]
Cu^{I}(acac—H) dpm		189 192	11 9 (11 62)	65 5 (65 86)	5 20 (5 34)			1593s 1585w(sh), 1577w(sh), 1498m
Cu^{I}(eaa—H) $(PPh_3)_2$	ether + pentane	128 5-129	9 1 (8 86)	70 0 (70 32)	5 62 (5 49)			1626s, 1583w, 1492m
Cu^{I}(eaa—H) (dpm)	ether	176 170	10 7 (11 01)	64 5 (64 51)	5 73 (5 12)			1627s, 1583w, 1570w, 1490m
Cu^{I}(eaa—H) (dpe)	benzene	(212)215 219dec	10 8 (10 78)	65 4 (65 02)	5.51 (5.63)			1619s, 1583w(sh), 1570w, 1493m
Cu^{I}(dem—H) $(PPh_3)_2$	benzene + ether	175 177	8 7 (8 50)	69 4 (69 11)	5 54 (5 53)			1636s, 1584w, 1500m
Cu^{I}(dem—H) (dpm)	acetone	(169)174-176	10 5 (10 47)	62 9 (63 30)	5 32 (5 48)			1640s, 1583w(sh), 1570w(sh), 1508m
Cu^{I}(dem—H) (dpe)	acetone	(200)210-216dec	10 0 (10 23)	63.9 (63 81)	5 54 (5 68)			1630s, 1584w, 1569w, 1548w, 1500m
Cu^{I}(eca—H) $(PPh_3)_2$	benzene + ether	165 166	9.1 (9 07)	70 0 (70 32)	5 09 (5 18)	1 96 (2 00)	2187s	1160s, 1583w, 1568w
Cu^{I}(eca—H)$_2$(dpe)$_3$	benzene + ether	214 216 (merged at 200°)	8 2 (8 28)	68 5 (68 31)	5 16 (5 17)	1.81 (1 81)	2146s	1618s, 1581w, 1568w(sh)

[a] acac = $CH_3COCH_2COCH_3$ eaa = $CH_3COCH_2COOC_2H_5$, dem = $H_5C_2OOCCH_2COOC_2H_5$, eca = $CNCH_2COOC_2H_5$ dpm = $Ph_2PCH_2PPh_2$, dpe = $Ph_2PCH_2CH_2PPh_2$

[b] Approximate average values of broad irregular bands

Cu(dpms$_2$ —H)·1/2 toluene (I)

dpms$_2$, $Ph_2P(S)CH_2(S)PPh_2$, (1.12 g, 2.5 mmol) was allowed to react for two days with a suspension of ArCu (2.5 mmol) in toluene (30 ml). The filtered yellow solution was then concentrated to give an ivory powder, m.p. 139° (dec). (Found: C, 61.4; H, 4.55; Cu, 11.7; S, 11.7; toluene 8.0; mol.wt. (1% w/w) 2208. Calcd.: C, 61.4; H, 4.52; Cu, 11.41, S, 11 51; toluene, 8.27%; mol.wt. 557.)

Reaction with HCl 0.2 g of I suspended in ether was treated with some drops of aqueous HCl (1/1) under vigorous stirring. The white solid formed, CuCl·dpms$_2$, was filtered and washed throughly with methanol. M p. 183-184. The IR spectrum is identical with that of needles obtained from cuprous chloride and dpms$_2$ in 1/1 ratio. (found: C, 55.6, H, 4.10; Cl, 6.4; Cu, 11.64; S, 11.3; mol.wt. (1.5% w/w in DCE) 981. CuCl·dpms$_2$ calcd C, 54.84; H, 4.05; Cl, 6 48, Cu, 11.60, S, 11.71%; mol.wt. 547.5.

[Cu(mn—H)]$_n$ (II)

mn, $NCCH_2CN$, (0.33 g, 5 mmol) was added to a stirred suspension of Cu Ar (5 mmol) in toluene (30 ml). The initial deep yellow colour disappeared gradually over a period of hours, while the stoichiometric amount of ArH went in solution. The pale cream powder, simultaneously formed, was collected and rinsed thoroughly with toluene. Even though dried in high vacuum it always contains a small constant amount of solvent, as confirmed by GLC. It darkens gradually starting at 200°, but does not melt even at 320°. (Found: C, 28.61; H, 0.93; Cu, 48.95; N, 21.4; toluene, 1.7. Cu(mn) 1.5% toluene calcd.: C, 28.98; H, 0 90; Cu, 48.67; N, 21.45; toluene 1.5%.

The product is practically insoluble in toluene, methylene chloride, dichloroethane, dimethoxyethane, sparingly soluble in acetone, ethanol, tetrahydro furan, dimethylformamide, and decomposes in dioxane

Reaction with pyridine 0.5 g of II were dissolved in a minimum of pyridine. Addition of ether to the deep orange solution precipitated a light brown powder, which was filtered and washed repeatedly with ether. The product darkens with time at room temperature, also in insert atmosphere, with loss of pyridine. (Found: C, 51,1; H, 3.5; Cu 25.32, N 19.6. $[Cu(mn—H)]_2py_3$ calcd· C, 51.00; H, 3.45, Cu, 25.70; N, 19.83%.

The product is practically insoluble in ether, ethanol and toluene, sparingly soluble in acetone and methylene chloride and decomposes in dimethoxyethane and dimethylformamide.

Reaction with triphenylphosphine A solution of mn (0.13 g, 2 mmol) and PPh_3 (1.05 g, 4 mmol) in ether (30 ml) was dropped into a suspension of ArCu (2 mmol) in ether (10 ml). The white solid rapidly formed was collected and washed repeatedly with ether. Recrystallization was from dichloroethane and ether. The solvent was removed in high vacuo. M.p. 216° (dec). (Found: C, 71.6; H, 4.70; Cu, 9.43; N, 4.31. $Cu(mn—H)(PPh_3)_2$ calcd.: C, 71.71; H, 4.78; Cu, 9.73; N, 4.29%.)

The compound is sparingly soluble at room temperature in the most common solvents, moderately so in hot chlorinated solvents or ethanol.

Reaction of ArCu with acac, eaa, dem and eca

The reaction between organocopper compounds and acac in ether immediately gave a deep red-brown solution. After a few minutes a copper mirror was deposited on the walls and a black precipitate was formed, whereas the mother liquor assumed a yellow-green colour. Extraction with THF of the black precipitate gave a residue of metallic copper and a blue solution, from which Cu(acac—H)$_2$ crystallized by concentration. In a similar manner Cu(eaa—H)$_2$ was obtained in the corresponding reaction but the reaction rate was slower, only 42% of the CuPh reacting after 12 h. With dem the reaction was even slower, only 20% of CuPh reacting after 24 h. The product with eca seems to be more stable. From the reaction we isolated a green-brown powder with a composition near to that required for Cu(eca—H), but which also evidently contained disproportionation products. The reaction, which was complete in ether in 24 h, did not proceed in toluene.

All the above reactions occurred rapidly in the presence of two equivalents of phosphine. The typical procedure to obtain the mixed complexes (Table 1) was the following: a suspension in toluene (10 ml) of CuPh (0.5 g, 3.5 mmol) was dropped into a toluene solution (20 ml) of 3.5 meq of the active hydrogen compound and 7 meq of the phosphine derivative. White precipitates were formed (reaction time: 1-8h), except in the case of eaa, whose very soluble complexes required concentration and overnight standing to precipitate. The complexes were recrystallized as specified in Table 1, avoiding prolonged heating.

Acknowledgements

Financial support from Italian National Research Council (CNR) is acknowledged. Microanalyses were carried out by Dr. E. Cebulec.

References

1 J F. Normant, Synthesis, (1972) 63 and references therein.
2 A. Camus, N Marsich G. Nardin and L. Randaccio, J Organometal Chem., 60 (1973) C39.
3 A. Cairncross and W A Sheppard, J. Amer. Chem. Soc., 90 (1968) 2186
V C R.McLoughlin and J. Thrower, Tetrahedron, 25 (1969) 5921
4 G Van Koten and J.G. Noltes, Chem. Commun., (1972) 59
5 M F. Lappert and R Pearce, J Chem. Soc. Chem. Commun , (1973) 24,
J.A.J. Jarvis, B T. Kilbourn and R Pearce, (1973) 475
6 H Schmidbaur, J. Adlkofer and W. Buchner, Angew. Chem., 85 (1973) 448.
7 P.G. Eller and P.W.R. Corfield, Chem. Commun , (1971) 105,
J.A. Tiethoff J.K Stalick, P W R Corfield and D.W. Meek, J. Chem. Soc. Chem. Commun , (1972) 1141;
J.A Tiethoff, J.K. Stalick and D W. Meek, Inorg. Chem., 12 (1973) 1170
8 D.W. Meek and P. Nicpon, J. Amer. Chem Soc , 87 (1965) 4951
9 T. Fujiyama and T. Simanouchi, Spectrochim Acta, 20 (1964) 829
10 M. Kubota and S R Schulze, Inorg. Chem., 3 (1964) 853
11 J H. Enemark and R.H. Holm, Inorg Chem., 3 (1964) 1516
12 G. Costa and G De Alti, Gazz. Chim. Ital., 87 (1957) 1273.
13 I A. Garbusova, V.T. Alexanjan, L.A. Leites, I R Golding and A.M. Sladkov, J. Organometal. Chem , 54 (1973) 341.
14 H.J. Coerver and C. Curran, J. Amer. Chem. Soc., 80 (1958) 3522.
15 S.K. Smirnov O G. Strukov S.S Dubov and L L Danilina, Zh Neorg Khim , 15 (1970) 1305

16 (a) F. Cariati and L. Naldini, Gazz. Chim. Ital., 95 (1965) 3
(b) R. Nast and W. H. Lepel, Chem. Ber., 102 (1969) 3224,
(c) D. Gibson, B.F.G. Johnson and J. Lewis, J. Chem. Soc. A, (1970) 367 and references therein,
(d) W.A. Anderson, A. J. Carty, G.J. Palenik and G. Schreiber, Can. J. Chem., 49 (1971) 761.
17 J. Klein and R. Levene, J.Chem. Soc. Perkin Trans II, (1973) 1971.
18 G. Behnke and K. Nakamoto, Inorg. Chem., 6 (1967) 440
19 N. Marsich, A. Camus and E. Cebulec, J. Inorg. Nucl. Chem., 34 (1972) 933.
20 J.M. Guss, R. Mason, I. Sotofte, G. Van Koten and J.G. Noltes, J. Chem. Soc. Chem. Commun., (1972) 447,
J.M. Guss, R. Mason, K.M. Thomas, G. Van Koten and J.G. Noltes, J. Organometal. Chem., 40 (1972) C79.
21 A. Camus and N. Marsich, J. Organometal. Chem., 14 (1968) 441.
22 K. Issleib and L. Baldauf, Pharm. Zentralh. Deut., 99 (1960) 329.