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Preparation and NMR studies of Mono- and Bis-phosphino Adducts of Bis(carboranyldithiocarboxylato)metal(II) Complexes of Nickel, Palladium and Platinum

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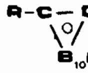
Reaction of the lithium salts of 1,2-carboranyldithiocarboxylic acids

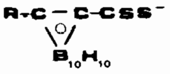


$\underset{B_{10}H_{10}}{R{-}C{-}C{-}CSSLi}$

($R = CH_3$, C_6H_5) with L_2MCl_2 ($M = Ni(II)$, $Pd(II)$, $Pt(II)$; L = tertiary phosphine) in ethereal solution gives neutral and diamagnetic mono- and/or bis-phosphino complexes of general formula $LM(S_2C\text{-}carb\text{-}R)_2$ and $L_2M(S_2C\text{-}carb\text{-}R)_2$, respectively. The tendency to form bis-phosphino adducts increases in going from nickel to platinum and appears also to depend on the type of the coordinated phosphine. By electronic and ^1H nmr spectroscopic evidence a five-coordinate structure was assigned to $LNi(S_2C\text{-}carb\text{-}R)_2$ and $L_2Ni(S_2C\text{-}carb\text{-}R)_2$ complexes in which the dithiocarboxylato groups exhibit bidentate and unidentate–bidentate modes of bonding, respectively. On the other hand, a four-coordination is attained by the bis-phosphino adducts of Pd(II) and Pt(II) through a unidentate mode of coordination of the dithio ligands. Furthermore, variable-temperature pmr studies on the $LPd(S_2C\text{-}carb\text{-}R)_2$ complexes showed rapid intramolecular interchange of the uni- and bidentate dithio ligands at ambient temperature.

Introduction

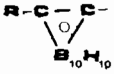
In a preliminary note [1] we have reported the preparation of some new complexes of the nickel triad elements containing 1,2-carboranyldithiocarboxylato anions



$\underset{B_{10}H_{10}}{R{-}C{-}C{-}CSS^-}$

($R = CH_3$, C_6H_5) as ligands. In particular, we have prepared bis-carboranyldithiocarboxylato complexes and their mono- and bis-phosphino adducts which are the first examples of complexes of this type. All of these compounds are non-electrolytes in solution and diamagnetic. Successively, in order to investigate further the carboranyldithiocarboxylato anions as ligands we have prepared a series of new mono- and bis-phosphino adducts of bis-carboranyldithiocarboxylato complexes of the nickel triad elements. The study of the properties of the carboranyldithiocarboxylato ligands is of interest for the following reasons: i) the dithiocarboxylato anions ($R\text{-}CSS^-$, R = alkyl or aryl) have been little investigated as ligands in comparison with other better-known dithioanions, such as $R_2NCS_2^-$, $R_2PS_2^-$, $(RO)_2PS_2^-$ or $ROCS_2^-$ [2, 3], and up to date only few examples of transition metal alkyl- or aryl-dithiocarboxylato complexes were reported [4, 5]. Moreover, the alkyl- and aryl-dithioanions appear to behave as bidentate ligands; ii) only two mono-phosphino adducts are hitherto known, namely those of the bis-dithiocumato- and bis-dithiobenzoato platinum(II) complexes; iii) bis-phosphino adducts of dithiocarboxylato complexes of the nickel triad elements are unknown.

Thus, we now report here the details of the preparation and characterization of several mono- and bis-phosphino adducts of bis-carboranyldithiocarboxylato complexes of Ni(II), Pd(II) and Pt(II) of general formulas $LM(S_2C\text{-}carb\text{-}R)_2$ and $L_2M(S_2C\text{-}carb\text{-}R)_2$, respectively, where L = tertiary phosphine and R-carb =



$\underset{B_{10}H_{10}}{R{-}C{-}C{-}}$

($R = CH_3$, C_6H_5).

Furthermore, the behaviour in solution of the obtained complexes was investigated by electronic and ^1H and ^{31}P nmr spectroscopies and evidence supporting both ligand exchange and unidentate/bidentate modes of bonding of the carboranyldithiocarboxylato groups is also reported.

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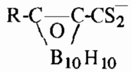
TABLE I. Analytical Data for Some Carboranyldithiocarboxylato Complexes.

	Compd[a]	Color	M.p.[b] (t/°C)	Found (%)				Calcd. (%)			
				C	H	P	S	C	H	P	S
I	$(Ph_3P)Ni(S_2C\text{-carb-}CH_3)_2$	blue-green	183	39.53	5.53	–	15.96	39.64	5.24	–	16.28
II	$(Ph_3P)Ni(S_2C\text{-carb-}C_6H_5)_2$	dark-green	135	47.67	4.99	–	11.38	47.41	4.97	–	14.04
III	$(Me_2PhP)Ni(S_2C\text{-carb-}CH_3)_2$	dark-green	157-159	29.05	5.67	4.99	19.20	28.95	5.62	4.67	19.33
IV	$(Me_2PhP)Ni(S_2C\text{-carb-}C_6H_5)_2$	blue-green	179-180	39.54	4.99	4.07	16.14	39.64	5.24	3.97	16.28
V	$(Me_2PhP)_2Ni(S_2C\text{-carb-}CH_3)_2$	orange-red	190	36.96	6.30	7.99	15.38	35.95	6.03	7.72	15.99
VI	$(Me_2PhP)_2Ni(S_2C\text{-carb-}C_6H_5)_2$	red-brown	178	43.90	5.80	6.47	13.52	44.10	5.66	6.69	13.85
VII	$(Ph_3P)Pd(S_2C\text{-carb-}CH_3)_2$	brown	187-188	37.40	4.85	3.63	15.30	37.38	4.94	3.71	15.35
VIII	$(Ph_3P)Pd(S_2C\text{-carb-}C_6H_5)_2$	brown	203	44.90	4.77	–	12.95	45.06	4.72	–	13.36
IX	$(Me_2PhP)Pd(S_2C\text{-carb-}CH_3)_2$	brown	177-179	26.56	5.82	4.32	17.98	27.01	5.25	4.35	18.03
X	$(Me_2PhP)Pd(S_2C\text{-carb-}C_6H_5)_2$	brown	159-160	37.03	4.98	–	–	37.37	4.95	–	–
XI	$(Me_2PhP)_2Pd(S_2C\text{-carb-}CH_3)_2$	green	165-166	33.16	6.44	–	–	33.93	5.69	–	–
XII	$(Me_2PhP)_2Pd(S_2C\text{-carb-}C_6H_5)_2$	yellow-green	184-186	41.79	5.60	6.28	13.10	42.0	5.39	6.37	13.08
XIII	$(Ph_3P)_2Pt(S_2C\text{-carb-}CH_3)_2$	olive-green	138	43.59	4.84	–	9.91	44.54	4.75	–	10.81
XIV	$(MePh_2P)_2Pt(S_2C\text{-carb-}CH_3)_2$	olive-green	175-176	38.46	4.94	5.96	12.08	38.44	4.93	5.83	12.07
XV	$(Me_2PhP)_2Pt(S_2C\text{-carb-}C_6H_5)_2$	yellow-green	190-191	38.47	5.19	5.82	11.94	38.44	4.92	5.82	12.07



a) $R\text{-carb-}CS_2^- = R\text{-}\underset{B_{10}H_{10}}{\underbrace{C\overset{O}{—}C}}\text{-}CS_2^-$ ($R = CH_3$ and C_6H_5); $Ph_3P = (C_6H_5)_3P$; $Me_2PhP = (CH_3)_2(C_6H_5)P$; $MePh_2P = (CH_3)(C_6H_5)_2P$;

b) All compounds melt with decomposition in a capillary tube sealed under vacuum.

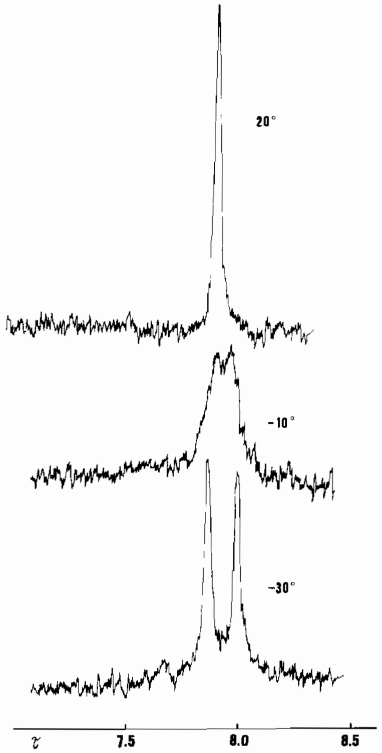
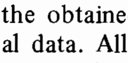


Figure 1. Variable-temperature ^1H nmr spectra in CH_2Cl_2 of $(Ph_3P)Ni(S_2C\text{-carb-}CH_3)_2$, I, in the methyl region.

Results and Discussion

Reaction of $1\text{-Li-2-R-1,2-}B_{10}C_2H_{10}$ (R = CH_3 (C_6H_5) with CS_2 in diethylether at 0 °C affords lithium salts of the 1,2-carboranyldithiocarboxylic acids (eq. 1).

$$\text{R-carb-Li} + CS_2 \xrightarrow[0\,^{\circ}C]{\text{ether}} \text{R-carb-CSS-Li} \qquad (1)$$

R-carb =  $\underset{B_{10}H_{10}}{\text{R-C}-\text{C-}}$ (R = CH_3, C_6H_5)

These lithium carboranyldithiocarboxylate salts react with the complexes L_2MCl_2 (M = Ni(II), Pd(II), Pt(II); L = tertiary phosphine) in ethereal suspension at room temperature to give bis-carboranyldithiocarboxylato derivatives containing either one or two phosphine ligands depending on the central metal atom and the type of the coordinated phosphine. Table I lists the obtained complexes with the pertinent analytical data. All of these complexes are diamagnetic either in solution or in the solid state and are non electrolytes in solution of CH_2Cl_2 at 25 °C.

Nickel(II) Complexes

When an ethereal solution of R-carb-CS_2Li (R= CH_3, C_6H_5) is treated with a suspension of $(Ph_3P)_2$-$NiCl_2$ at room temperature the monophosphino complexes $(Ph_3P)Ni(S_2C\text{-carb-R})_2$, I or II, are merely obtained. On the other hand, a mixture of mono-phosphino (III, IV) and bis-phosphino (V, VI) derivatives appears to be the product of the reaction between $(Me_2PhP)_2NiCl_2$ and dithiocarboxylate salts. The monophosphino complexes are stable either in the solid state or in solution, whereas the bisphosphino derivatives are stable in solution only under inert atmosphere. Molecular weight measurements indicate that the complexes I, II, V and VI are monomeric in solution. On the other hand, the poor solubility of II and III prevented any molecular weight determinations.

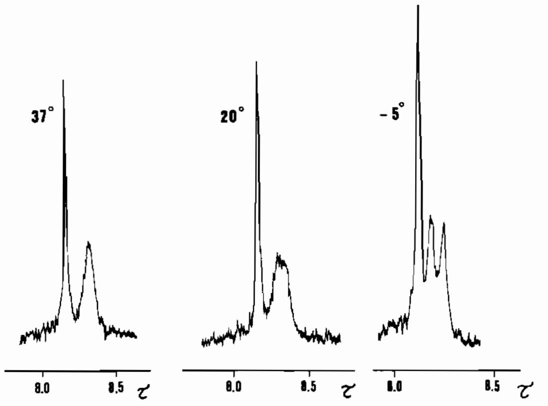
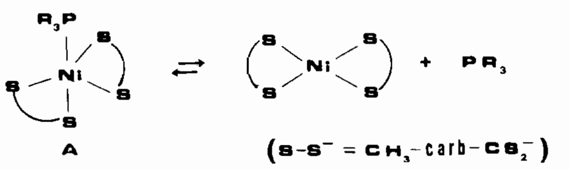


Figure 2. Variable-temperature ^1H nmr spectra in CH_2Cl_2 of $(Me_2PhP)Ni(S_2C\text{-carb-}CH_3)_2$, III, in the methyl region.

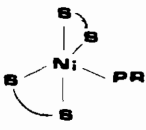
The ^1H nmr spectrum of $(Ph_3P)Ni(S_2C\text{-carb-}CH_3)_2$, complex I, in CH_2Cl_2 at room temperature exhibits a single resonance at τ 7.97 due to the carborane methyl protons of the dithiocarboxylato ligands. As the temperature is lowered this resonance broadens until at –30 °C two sharp singlets of the same intensities centered at τ 7.95 and τ 8.09, respectively, are observed (Fig. 1). This temperature dependence is reversible. The chemical shift and line shape of the carborane methyl proton resonances are unaffected by addition of free Ph_3P. The ^{31}P nmr spectrum of complex I in $CDCl_3$ shows a single resonance at +36.1 ppm at room temperature. Addition of 2 equiv of Ph_3P gives an additional broad resonance at –5.4 ppm whereas the resonance of the coordinated phosphine remains unchanged. On lowering the temperature to –30 °C, sharp resonances at +36.1 and at –6.6 ppm, due to the bound and free ligand respectively, are observed. The cumulative ^1H and ^{31}P nmr data for this complex may be explained with the assumption of a partial phosphine ligand dissociation and a fast intermolecular ligand exchange process occurring at room temperature. The dissociation should involve an equilibrium between a trigonal-bipyramidal five-coordinate and a four-coordinate species (eq. 2).



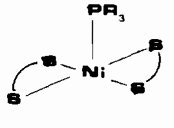
Moreover, to account for the carborane methyl resonances of the same intensities separated by 0.14 ppm shown by complex I at low temperature, we think this observation may be consistent with the presence of the "frozen-out" species A in which a phosphine ligand in apical position makes magnetically inequivalent the methyl groups of the two bidentate dithio ligands [3].

A phosphine ligand dissociation and a fast intermolecular exchange process are also suggested to explain the temperature dependence of the phosphine methyl proton resonance observed for the complexes III and IV. The ^1H nmr spectrum (in CH_2Cl_2) of complex III shows at room temperature a singlet at τ 8.12 due to the carborane methyl protons of the dithioligands and a broad resonance centered at τ 8.28 attributed to the phosphine methyl protons. On cooling, the latter resonance broadens until at -5 °C it forms a 1:1 sharp doublet centered at τ 8.31 (J_{PH} = 8.3 Hz), whereas the singlet at τ 8.16 remains unchanged (Fig. 2). Similarly, the phosphine methyl proton resonance for IV (in CS_2:$CDCl_3$ = 2:1) appears at room temperature as a broad singlet (τ = 8.71) and at -20 °C as a sharp 1:1 doublet (τ = 8.73; J_{PH} = 9.6 Hz).

The different temperature-dependence of the carborane methyl proton resonances between the complexes I and III may be due to a different stereochemistry of the "frozen-out" species. Thus a five-coordinate structure of the type B or C could explain the carborane methyl proton magnetic equivalence observed in the low-temperature pmr spectrum of complex III.



B



C

As spectrophotometric experiments in benzene solution showed that the complexes I–IV follow Beer's law when the concentrations are varied within the 1 X 10^{-3}–5 X 10^{-5} *M* range, the reaction equilibrium must be very far to the left [6].

While both the dithio ligands appear to behave as bidentate in the monophosphino adducts (I–IV), the same ligands exhibit different modes of bonding in the bisphosphino derivatives. Thus, the ^1H nmr spectrum of complex V, $(Me_2PhP)_2Ni(S_2C\text{-carb-}CH_3)_2$, shows at 30 °C in $CDCl_3$ two sharp singlets centered at τ 8.11 and 8.89, attributed to the carborane methyl protons, a broad singlet centered at τ 8.49 and two 1:1 doublets at τ 7.41 (J(PH) = 11.4 Hz) and 7.71 (J(PH) = 13.3 Hz) due to the phosphine methyl protons. On cooling the line shape of the carborane methyl proton resonance remains unchanged, but the singlet centered at τ 8.49, due to the phosphine methyl protons, broadens and collapses and finally at +10 °C two overlapping sharp 1:1 doublets centered at τ 8.37 (J(PH) = 8.7 Hz) and τ 8.46 (J(PH) = 9.1 Hz), respectively, are observed (Fig. 3). This temperature-dependent behavior is reversible. The large difference between the chemical shifts of the carborane methyl protons of the two dithio ligands ($\Delta\tau$ = 0.78 ppm) exhibited by V can be explained assuming that the observed chemical inequivalence induced by a different mode of bonding of the two dithio ligands in this bis-carboranyldithiocarboxylato complex. Thus we suggest for the complex V a five-coordinate structure in which one dithiocarboxylato group acts as bidentate and the other as unidentate. On account of the temperature-dependent pmr spectrum shown by the phosphino methyl protons we propose an inter-

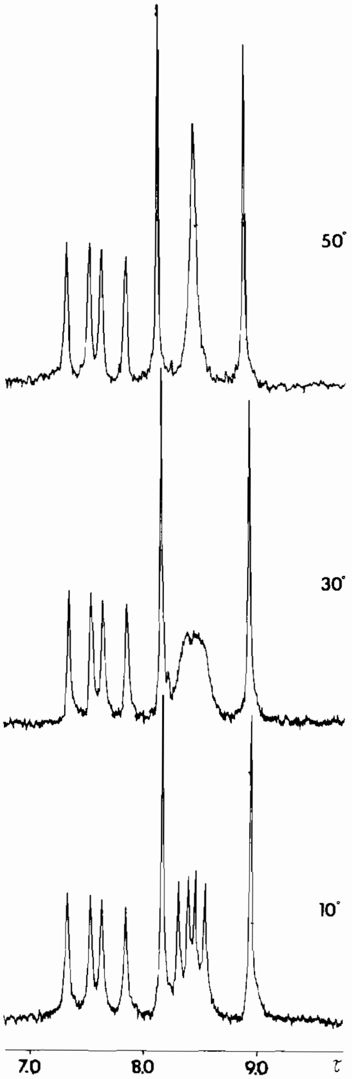


Figure 3. Variable temperature ^1H nmr spectra in $CDCl_3$ of $(Me_2PhP)_2Ni(S_2C\text{-carb-}CH_3)_2$, V, in the methyl region.

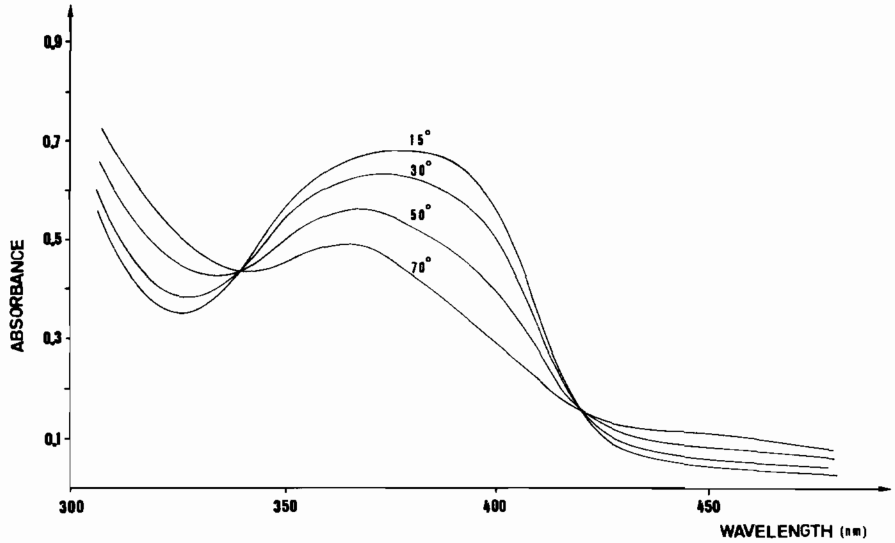


Figure 4. Absorption spectra of 9.4 × 10^{-5} *M* $(Me_2PhP)_2Pd(S_2C\text{-carb-}CH_3)_2$, X, at various temperatures in benzene (5 mm cell).

molecular exchange process consistent with the assumption that this five-coordinate complex is dissociatively unstable with respect to the equilibrium reaction 3.

$$(Me_2PhP)_2Ni(S_2C\text{-carb-R})_2 \rightleftarrows (Me_2PhP)Ni(S_2C\text{-carb-R})_2 + Me_2PhP \qquad (3)$$

The loss of P–H coupling shown at higher temperature by the protons of one phosphine ligand is indicative of a fast intermolecular exchange process involving only one phosphine group. However, the equilibrium 3 should be very far to the left since detectable dissociation of V in solution is ruled out by the fact that Beer's law is obeyed at concentrations ranging from 1 × 10^{-2} to 5 × 10^{-4} *M* [7]. Finally, the observed chemical shift inequivalence of the phosphine methyl protons is in agreement with a structure in which the two phosphorus atoms are prochiral centers. There are no molecular symmetry planes passing through these prochiral center atoms and thus geminal methyl groups at both these centers are diastereotopic [8].

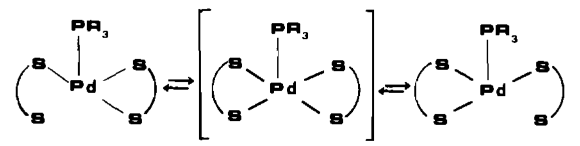
On the basis of the ^{1}H nmr and UV–visible spectra, a five-coordinate structure and a behaviour similar to that shown by complex V in solution can be also suggested for complex VI [9].

Palladium(II) Complexes

The complex *cis*-$(Ph_3P)_2PdCl_2$ reacts with R-carb-CS_2Li (R = CH_3, C_6H_5) yielding merely the monophosphino derivatives $(Ph_3P)Pd(S_2C\text{-carb-R})_2$, VII and VIII. On the other hand, the analogous reaction with the complex *cis*-$(Me_2PhP)_2PdCl_2$ gives bis-phosphino adducts of general formula $(Me_2PhP)_2Pd(S_2C\text{-carb-R})_2$, XI and XII, together with smaller amounts of the corresponding monophosphino complexes IX and X. Conversely, good yields of the latter monophosphino adducts can be obtained by treating the lithium carboranyldithiocarboxylates with $(Me_2PhP)_2Pd_2Cl_4$. Molecular weight determinations show that the monophosphino complexes VII–X are monomeric in solution. On the other hand, the poor solubility of the bis-phosphino adducts prevented any molecular weight determinations.

Detectable dissociation of the mono-phosphino adducts VII–X is ruled out by the fact that Beer's law is obeyed at concentrations from 10^{-3} to 10^{-5} *M*. Moreover, while the electronic spectra of VII and VIII are unaffected by addition of large excess of free Ph_3P, the addition of small amounts of Me_2PhP to the solution of complexes IX and X causes disappearance of the absorption bands at 450 and 550 nm, typical of the monophosphino adducts. The electronic spectra of the bis-phosphino adducts, XI and XII, in benzene or 1,2-dichloroethane solutions at 25 °C show no absorptions attributable to the corresponding mono-phosphino complexes. However, on heating absorptions appear at 450 and 550 nm which increase with increasing temperature and isosbestic points are observed when the temperature is varied from 15 to 70 °C (Fig. 4). These results suggest that phosphine ligand dissociation occurs in solution, whose extent is very small even at 70 °C [10].

The ^{1}H nmr spectra of VII and IX in CH_2Cl_2 at 40 °C exhibit a sharp singlet (VII: τ = 8.06; IX: τ = 7.99) due to the carborane methyl protons of the dithio ligands. The spectrum of complex IX shows also a 1:1 doublet centered at τ 8.14 (J(PH) = 11.0 Hz) due to the phosphine methyl protons, which appears to be independent of temperature from 40 to −80 °C [11]. On the other hand, the singlet (carborane methyl proton resonance) exhibited by both the complexes VII and IX shows a progressive broadening when the temperature is lowered until −110 °C (in CS_2 solution) One explanation of these observed pmr spectra suggests that an equilibrium exists in solution between two square planar, open chelate ring structures, via a five-coordinate intermediate, as shown in the following scheme



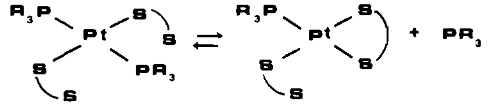
Thus, a fast intramolecular exchange process produces the apparent equivalence of the carborane methyl groups of the dithio ligands, as observed above −80 °C However, this rate of rearrangement is probably too fast even at −110 °C and thus only a light broadening of the singlet was observed [12]

The ^1H nmr spectrum (CD_2Cl_2) of the bis-phosphino adducts XII exhibits at room temperature a broad signal centered at τ 8 96 due to the phosphine methyl protons As the temperature is lowered this signal broadens and finally at −30 °C a well-defined triplet centered at τ 9 09 (J_{PH}(apparent) = 3 6 Hz) is observed The pattern at low temperature is consistent with a square-planar structure having two phosphine ligands in mutual *trans* position and two unidentate dithio ligands The loss of P–H coupling observed at room temperature is attributable to a partial phosphine ligand dissociation accompanied by a fast intermolecular ligand exchange process

Platinum(II) Complexes

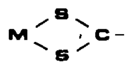
Bis-phosphino only, $L_2Pt(S_2C\text{-carb-}R)_2$, XIII–XV, are the products of the reaction between *cis*-L_2PtCl_2 (L = Ph_3P, $MePh_2P$, Me_2PhP) and lithium carboranyldithiocarboxylate Complex XIV is not soluble in the most common organic solvents and it prevented any investigation of its behaviour in solution Complexes XIII and XV are moderately soluble and their molecular weight determinations and UV–visible spectra indicate that appreciable dissociation of phosphine ligand occurs in solution

The ^{31}P nmr spectrum of XIII (in $CDCl_3$) exhibits a broad singlet centered at +4 3 ppm at room temperature On cooling the solution below −30 °C, the signal sharpens and finally at −40 °C a sharp singlet flanked by symmetrical satellites due to the coupling with ^{195}Pt nucleus (J_{Pt-P} = 3160 Hz) is observed at +12 2 ppm Complex XV shows a temperature-dependent ^1H nmr spectrum At room temperature (in $CDCl_3$) a broad singlet centered at τ 8 91 due to the phosphine methyl proton resonance was observed. If the solution is cooled, this signal broadens and finally at 0 °C a sharp triplet (τ = 8 99, J_{PH} = 3 6 Hz) symmetrically flanked by satellites due to the coupling with the ^{195}Pt nucleus (J^3_{Pt-H} = 26 5 Hz) is observed The low-temperature nmr spectra for both XIII and XV are consistent with the presence of "frozen-out" square-planar species having the platinum(II) atom coordinated by two unidentate dithio ligands and by two phosphine ligands in mutual *trans* position The most likely explanation of the temperature-dependent nmr spectra of these complexes assumes phosphine dissociation (eq 4) accompanied by a fast intermolecular exchange process of free and complexed ligand This accounts also for the loss of Pt–P, Pt–H and P–H couplings observed at room temperature



(4)

Further evidence for the equilibrium reaction 4 is given by the observation that the solution electronic spectra of complexes XIII and XV are modified by addition of free phosphine ligand In fact, the UV–visible spectra of both these complexes show a low-energy absorption band (450 nm) assignable to a transition within the conjugate



group which is suppressed by addion of free ligand

In conclusion, collective UV–visible and ^1H and ^{31}P nmr spectroscopic evidence indicates that the bis-phosphino adducts of the biscarboranyldithiocarboxylato complexes of Ni(II), Pd(II) and Pt(II) are dissociatively unstable with respect to the phosphine ligands according to the equilibrium reactions reported above In addition, the ligand dissociation appears to be accompanied by an intermolecular phosphine exchange process as shown by the temperature-dependent nmr spectra However, it is to be noted that the geometry of the various species formed in solution could be not unequivocally determined from electronic spectra In fact, limitations to their interpretation are placed by the intense pink–red color of the free dithio ligands which masks spectral changes occurring on complexation and thus investigations of the metal chromophores are often prevented

Systematic efforts to estimate the equilibrium constants, or instability constants, for these complexes in solution and to evaluate the kinetic parameters of the ligand exchange processes are now in progress

Experimental

Materials

The solvents used were of reagent grade quality and were dried and degassed before use The complexes

$(Ph_3P)_2NiCl_2$ [13], *cis*-$(Ph_3P)_2PdCl_2$ [14], *cis*-$(Ph_3P)_2PtCl_2$ [15], $(Me_2PhP)_2NiCl_2$ [16], $(Me_2PhP)_2PdCl_2$ [17], $(Me_2PhP)_2Pd_2Cl_4$ [17], *cis*-$(MePh_2P)_2PtCl_2$ [18] and *cis*-$(Me_2PhP)_2PtCl_2$ [18] were prepared by literature methods. The lithium-carborane derivatives were prepared by treating 1-H-2-R-1,2-$B_{10}C_2H_{10}$ (R = CH_3, C_6H_5) with lithium buthyl as reported in the literature [19]. All reactions were carried out under dry nitrogen.

Physical Measurements

The ^1H nmr spectra were recorded at 60 MHz and 90 MHz with WP-60 FT NMR and HFX-90 Bruker Spectrometers, respectively. ^1H chemical shifts *vs.* internal TMS are ± 0.02 ppm; J_{PH} values are ± 0.2 Hz; ^{31}P chemical shifts *vs.* external 85% H_3PO_4 (downfield positive) are ± 0.1 ppm; J_{Pt-P} values are ±1 Hz. Electronic spectra were recorded on an Optica CF4NJ spectrophotometer. Molecular weights were measured with a Mechrolab vapor-phase Osmometer Model 301 B.

Preparation of Ligands

Solutions of lithium carboranyldithiocarboxylate are prepared by treating an ethereal solution (*ca.* 0.3 *M*) of 1-Li-2-R-1,2-$B_{10}C_2H_{10}$ (R = CH_3, C_6H_5) with a stoichiometric amount of CS_2 at 0 °C under inert atmosphere. The reaction mixture immediately turns to intense pink color. Attempts to isolate the lithium methylcarboranyldithiocarboxylate as crystals were unsuccessful and only a uncrystallizable oil was obtained. Conversely, in the case of the lithium phenylcarboranyldithiocarboxylate pink crystals were easily obtained on concentration of the reaction mixture. These crystals were separated by filtration and washed with n-hexane. Yield 90%; mp. 96 °C (dec. under vacuum). *Anal.* Calcd. for $C_9H_{15}B_{10}S_2Li$: C, 35.75; H. 4.96; S, 21.22. Found: C, 35.40; H, 5.05; S, 22.10%.

Preparation of Complexes

The most convenient preparation of carboranyldithiocarboxylato complexes is the reaction between a suspension of the appropriate chloro complex of the given metal in diethyl ether and *ad hoc* prepared solution of lithium salt of the suitable carboranyldithiocarboxylic acid.

$(Ph_3P)Ni(S_2C$-carb-$CH_3)_2$, I

A solution of CH_3-carb-CS_2Li (4.67 mmol) in 20 ml of diethyl ether was added to a suspension of 1.2 g (1.8 mmol) of $(Ph_3P)_2NiCl_2$ in 15 ml of diethylether at room temperature. The reaction mixture was stirred for 24 hr. The lithium chloride formed was filtered off and the obtained solution was evaporated to dryness under reduced pressure. The solid product was purified by recrystallization from CH_2Cl_2/CH_3OH to give 1.0 g (yield 64%) of blue–green crystals of I, m.p. 183 °C dec. M.wt.: calcd, 788; found, 840 (in 1,2-dichloroethane).

$(Ph_3P)Ni(S_2C$-carb-$C_6H_5)_2$, II

This complex was prepared as I. The crude product was recrystallized from tetrahydrofurane/ethanol. The yield of pure dark–green crystals of II was 53%; m.p. 134–135 °C, dec. M.wt.: calcd, 912; found, 950 (in THF).

$(Me_2PhP)Ni(S_2C$-carb-$CH_3)_2$, III, and $(Me_2PhP)_2Ni(S_2C$-carb-$CH_3)_2$, V

A solution of CH_3-carb-CS_2Li (7.35 mmol) in diethyl ether (20 ml) was added dropwise to a suspension of 1.0 g (2.45 mmol) of $(Me_2PhP)_2NiCl_2$ in diethylether (10 ml) at room temperature. After being stirred for 1 hr, the reaction mixture was filtered to remove the lithium chloride formed and then evaporated to dryness under reduced pressure. The crude product was dissolved in a minimum of CH_2Cl_2 and then by addition of n-hexane a red powder was precipitated which was separated by filtration. The solution was evaporated under reduced pressure to a green solid which was purified by double recrystallization from CH_2Cl_2/C_2H_5OH to give 0.17 g (yield 10%) of dark green crystals of pure monophosphino derivative III; m.p. 157–159 °C, dec.

The red powder was purified by recrystallization from CH_2Cl_2/C_2H_5OH giving the pure bis-phosphino-derivative V, as orange–red microcrystals (0.92 g; yield 47%); m.p. 184–185 °C, dec. M.wt.: calcd., 802; found, 790 (in C_6H_6).

$(Me_2PhP)Ni(S_2C$-carb-$C_6H_5)_2$, IV, and $(Me_2PhP)_2Ni(S_2C$-carb-$C_6H_5)_2$, VI

As the complex III and V, these were prepared on treating a suspension of $(Me_2PhP)_2NiCl_2$ (1 g, 2.44 mmol) in diethylether (10 ml) with C_6H_5-carb-CS_2Li (7.35 mmol) in diethyl ether (10 ml) at room temperature. The reaction mixture was stirred for 1.5 hr. During the reaction a solid was formed which was separated by filtration, washed with diethyl ether to give a dark-green crude product. This product was treated with 10 ml of CH_2Cl_2 and then by filtration a brown solution and a green solid were obtained. The latter was purified by recrystallization from THF–C_2H_5OH to give 0.59 g (yield 30%) of pure IV, blue–green crystals; m.p. 179–180 °C dec.

On addition of ethanol to the solution, a red–brown product was precipitated which was further purified by recrystallization from CH_2Cl_2–C_2H_5OH to give 0.45 g (yield 20%) of the pure bis-phosphino derivative VI, red–brown crystals, m.p. 170 °C, dec. M.wt.: calcd, 926; found 930 (C_6H_6).

$(Ph_3P)Pd(S_2C$-carb-$CH_3)_2$, VII

A solution of 4.26 mmol of CH_3-carb-CS_2Li in 15 ml of diethyl ether was added to a suspension of

1.0 g (1.42 mmol) of $(Ph_3P)_2PdCl_2$ in 15 ml of ether at room temperature. After being stirred for 1 hr, the reaction mixture was filtered and the resulting solution was evaporated to a dark solid. This crude product was dissolved in 10 ml of CH_2Cl_2 and then by addition of CH_3OH a dark-red product was obtained which was further purified by recrystallization from CH_2Cl_2/CH_3OH to give 0.74 g (yield 63%) of pure VII, brown crystals, m.p. 187–188 °C, dec. M.wt.: calcd, 835; found 830 (in 1,2-dichloroethane).

$(Ph_3P)Pd(S_2C\text{-carb-}C_6H_5)_2$, VIII

This complex was prepared as VII and a yield of 43% of VIII, as brown crystals, was obtained; m.p. 202–203 °C, dec. M.wt.: calcd, 960; found, 910 (in 1,2-dichloroethane).

$(Me_2PhP)Pd(S_2C\text{-carb-}CH_3)_2$, IX, and $(Me_2PhP)_2Pd(S_2C\text{-carb-}CH_3)_2$, XI

A solution of 5.5 mmol of CH_3-carb-CS_2Li in 10 ml of diethylether was added to a suspension of 0.58 g (0.92 mmol) of $(Me_2PhP)_2Pd_2Cl_4$ in 10 ml of ether at room temperature. The reaction mixture was stirred for 3 hr. During the reaction a precipitate was formed which was separated by filtration, washed with CH_3OH and recrystallized from CH_2Cl_2/n-hexane giving 0.41 g (yield 62%) of the pure monophosphinoderivative, IX, deep-brown crystals; m.p. 177–179 °C, dec. M.wt.: calcd, 711; found 720 (in 1,2-dichloroethane). On concentration of the filtered solution and on addition of ethanol, the bis-phosphino derivative, XI, was precipitated as green solid. This crude product was recrystallized from CH_2Cl_2/C_2H_5OH to give 0.1 g of pure XI, green crystals; m.p. 165–166 °C dec.

$(Me_2PhP)Pd(S_2C\text{-carb-}C_6H_5)_2$, X

A solution of 0.3 g (0.31 mmol) of complex XII in 20 ml of tetrahydrofurane and 15 ml of diethyl ether was stirred for 2 hr at room temperature. The mixture obtained was then evaporated to dryness under reduced pressure. The solid product so obtained was dissolved by addition of 8 ml of CH_3OH. On addition of diethyl ether the parent complex XII precipitated and it was filtered off. The resulting solution was evaporated under reduced pressure to brown solid which was further purified by recrystallization from CH_2Cl_2/n-hexane. The yield of pure X, brown crystals, was 0.1 g (37%); m.p. 159–160 °C, dec.

$(Me_2PhP)_2Pd(S_2C\text{-carb-}C_6H_5)_2$, XII

A solution of 3.31 mmol of C_6H_5-carb-CS_2Li in 10 ml of diethyl ether was added to a suspension of 0.5 g (1.1 mmol) of $(Me_2PhP)_2PdCl_2$ in 10 ml of ether at room temperature. The reaction mixture was stirred for 1 hr. The precipitate formed was separated by filtration, washed with methanol and purified by recrystallization from CH_2Cl_2/CH_3OH. The yield of pure XII, yellow–green crystals, was 0.64 g (60%); m.p. 184–186 °C dec.

$(Ph_3P)_2Pt(S_2C\text{-carb-}CH_3)_2$, XIII

To a suspension of 1.5 g (1.8 mmol of *cis*-$(Ph_3P)_2PtCl_2$ in 20 ml of diethyl ether was added a solution of 5.7 mmol of CH_3-carb-CS_2Li in 20 ml of ether at room temperature. The reaction mixture was stirred for 3 hr. During the reaction dark-green crystals were formed which were separated by filtration and purified by recrystallization from CH_2Cl_2/CH_3OH to give 1.5 g (yield 66%) of pure XIII, olive–green crystals; m.p. 138 °C dec.

$(MePh_2P)_2Pt(S_2C\text{-carb-}CH_3)_2$, XIV

A solution of 2.25 mmol of CH_3-carb-CS_2Li in 10 ml of diethyl ether was added to a suspension of 0.5 g (0.75 mmol) of $(MePh_2P)PtCl_2$ in 10 ml of ether at room temperature. After being stirred for 3 hr, the precipitate formed was separated by filtration and washed with 15 ml of CH_3OH. This crude product was purified by recrystallization from THF/C_2H_5OH to give 0.65 g (yield 80%) of olive-green crystals of pure XIV: m.p. 175–176 °C dec.

$(Me_2PhP)_2Pt(S_2C\text{-carb-}C_6H_5)_2$, XV

As the complex XIV, this was prepared from 2.76 mmol of C_6H_5-carb-CS_2Li and 0.5 g (0.92 mmol) of $(Me_2PhP)_2PtCl_2$. The purification of the crude was carried out by recrystallization from CH_2Cl_2/CH_3OH. The yield of pure XV, yellow-green crystals, was 0.75 g (77%); m.p. 190–191 °C.

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6 An upper limit of *ca.* 5×10^{-7} *M* can be calculated for the dissociation equilibrium constant

$$(R_3P)Ni(S_2C\text{-carb-}R)_2 \xrightleftharpoons{K_d} Ni(S_2C\text{-carb-}R)_2 + R_3P$$

by assuming that a 10% dissociation in the most dilute solution would have been detectable.

7 A $K_d < 10^{-6}$ *M* for complex V can be estimated, assuming that a 5% dissociation would be detected.

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9 The ^1H nmr spectrum of complex VI in $CDCl_3$ at 40 °C exhibits two 1:1 doublets centered at τ 7.88 (J_{PH} = 12.0 Hz) and at τ 8.16 (J_{PH} = 13.0 Hz) and a singlet at τ 8.66 due to the methylphosphine protons. At +10 °C these resonances appear as four 1:1 doublets centered at τ 7.45 (J_{PH} = 11.4 Hz), 8.33 (J_{PH} = 12.0 Hz), 8.58 (J_{PH} = 8.6 Hz) and 8.76 (J_{PH} = 9.0 Hz), respectively.

10 A $K_d < 10^{-9}$ *M* in C_6H_6 for XI can be calculated by the absorbance at 450 nm being known the extinction coefficients of the corresponding mono-phosphino derivatives (λ_{max} = 450 nm (sh); ϵ_{max} = 3080 cm^{-1} M^{-1}).

11 The ^1H nmr spectrum of X in CH_2Cl_2 at 40 °C exhibits a sharp 1:1 doublet centered at τ 8.48 (J_{PH} = 11.0) attributed to the phosphine methyl protons. The behavior of this ^1H nmr spectrum is unaffected by the temperature between +40 °C and –80 °C.

12 A facile unidentate–bidentate exchange process of dithio ligands was also suggested for the complexes $[M(S\text{-}S)_2\text{-}ER'_3]$, M = Pd, Pt; S-S = $R_2PS_2^-$; ER'_3 = PR'_3, AsR'_3, by D. F. Steele and T. A. Stephenson, *J. Chem. Soc., Dalton,* 2124 (1973).

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