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CATIONIC ORGANOMETALLIC COMPLEXES WITH HEXAALKYLBORAZINES

I. SYNTHESIS AND REACTIVITY OF CATIONIC HEXAMETHYLBORAZINERHODIUM COMPLEXES WITH CARBONYL, ETHYLENE AND DIOLEFINS AS LIGANDS

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Summary

The PF_6 salts of the new cationic hexamethylborazinerhodium(I) complexes of general formula $[Rh(Me_3B_3N_3Me_3)(LL')]^+$ (LL′ = 1,5-cyclooctadiene, norbornadiene, tetrafluorobenzobarrelene, trimethyltetrafluorobenzobarrelene, L = L′ = ethylene, CO) have been prepared from the reaction between $[RhCl(LL')]_2$, $Me_3B_3N_3Me_3$, and $AgPF_6$ in dichloromethane. These complexes are very labile, undergoing rapid ring ligand exchange in solution with σ- and π-donor ligands. The synthesis of $[Rh(\eta^6\text{-naphthalene})(COD)]PF_6$ is also described. The properties and NMR and IR spectroscopic characteristics of the new compounds are briefly discussed.

Introduction

Borazines have the general formula $R_3B_3N_3R'_3$ and can be formulated as either cyclic triamines, (a), or as heterocycles, (b), with a delocalized π-electron system isoelectronic with benzene derivatives.

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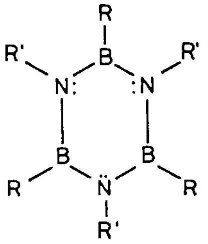
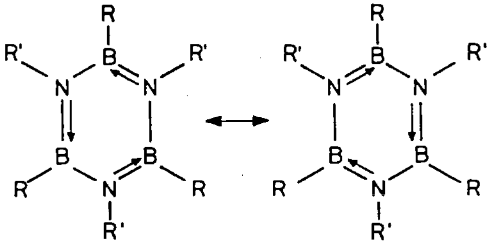


(a)



(b)

Structural studies have shown that the borazine ring is essentially planar. However, chemical evidence indicates that the nitrogen atoms in the borazine ring retain their basic character [1,2]. Thus it would be expected that the parent borazine and its derivatives could form metal–ring complexes similar to those of the corresponding hexahydrotriazine [3] or of benzene or other arenes [4,5].

It was first shown by molecular orbital calculations that complexes of the type $[M(CO)_3(\eta^6\text{-borazine})]$ (M = Cr, Mo, W) should be stable [6,7]. This conclusion was partially confirmed by the synthesis of $[Cr(CO)_3(R_3B_3N_3R'_3)]$ (R, R′ = H, Me, Et, Pr, i-Pr) [8–12] and $[Mo(CO)_3(R_3B_3N_3R'_3)]$ (R,R′ = Me, Et) [13]. Measurements of the bond enthalpy contribution $B_3N_3R_6Cr$ (R = Me, Et) for the $[Cr(CO)_3(B_3N_3R_6)]$ complexes gave values approximately one half of that for C_6R_6Cr in the corresponding $[Cr(CO)_3(\eta^6\text{-}C_6R_6)]$ complexes. A reasonable explanation for this result is that whereas the donor properties of hexaalkylborazines and alkylbenzenes are probably comparable, the acceptor properties are likely to be markedly different [14]. This may explain why there is such an extensive chemistry for arene-metal derivatives, whereas knowledge of borazinemetal compounds is still restricted to complexes containing the $Cr(CO)_3$ or $Mo(CO)_3$ group.

If the metal–$R_3B_3N_3R'_3$ bond is generally weak, it can be assumed that the lability of compounds $[ML_n(R_3B_3N_3R'_3)]$ with respect to ring ligand exchange is influenced more by thermodynamic than by kinetic effects. This lability makes it difficult to find suitable precursors for the synthesis of borazinemetal derivatives. On the other hand, compounds with a borazinemetal unit should be good starting materials for the synthesis of complexes with stronger metal–ligand bonds. This has been confirmed by the synthesis of anionic chromium carbonyl complexes containing Cr–Sn bonds [15], and more recently by the isolation of cationic heterodinuclear Rh^I/Cr^0 complexes containing diphenylmethane as bridging ligand [16].

The studies of the synthesis of these binuclear compounds now raises the question of whether it would be possible to obtain cationic hexamethylborazinemetal derivatives of the type $[Rh(Me_3B_3N_3Me_3)(LL')]^+$ similar to the corresponding arene complexes $[Rh(\eta^6\text{-arene})(LL')]^+$ (LL′ = diolefin; L = L′ = ethylene, CO). In general these complexes have been obtained by the reaction of $[RhCl(LL')]_2$ (LL′ = 1,5 cyclooctadiene (COD), norbornadiene (NBD), tetrafluorobenzobarrelene (TFB), trimethyltetrafluorobenzobarrelene (Me_3TFB); L = L′ = ethylene, CO) with AgA (A = BF_4, ClO_4, PF_6) in the presence of the arene ligand in a weakly coordinating solvent such as $(CH_3)_2CO$, THF or CH_2Cl_2. These solvents generate cationic intermediate species of the general type $[RhLL'(S)_x]^+$, containing labile Rh–S bonds [17–21]. It was this lability which seemed promising for the synthesis of cationic borazinerhodium complexes, which should be formed in the same way as the corresponding arene derivatives.

Results and discussion

The compounds $[Rh(Me_3B_3N_3Me_3)(LL')]PF_6$ were prepared according to eq. 1, where LL' = diolefins: 1,5-cyclooctadiene (COD) (I), norbornadiene (NBD) (II), tetrafluorobenzobarrelene (TFB) (III), trimethyltetrafluorobenzobarrelene (Me_3TFB) (IV); or L = L' = ethylene (V), CO (VI)).

$$[RhCl(LL')]_2 + 2\ AgPF_6 + 2\ Me_3B_3N_3Me_3 \xrightarrow{CH_2Cl_2} 2[Rh(Me_3B_3N_3Me_3)(LL')]PF_6 + 2\ AgCl \qquad (1)$$
$$\text{(I–VI)}$$

The naphthalene derivative $[Rh(\eta^6\text{-}C_{10}H_8)(COD)]PF_6$ (VII) was similarly obtained according to eq. 2:

$$[RhCl(COD)]_2 + 2\ AgPF_6 + 2\ C_{10}H_8 \xrightarrow{(CH_3)_2CO} 2[Rh(\eta^6\text{-}C_{10}H_8)(COD)]PF_6 + 2\ AgCl \qquad (2)$$

The preparation of the complexes I, II, IV and VII was carried out at room temperature using an excess of the hexamethylborazine or naphthalene ligand in the presence of the stoichiometric amount of $AgPF_6$. In contrast, the compounds III, V and VI had to be prepared at low temperature (−40°C), but under otherwise similar conditions. The complexes were obtained as microcrystalline solids, very sensitive to moisture. The molar conductivities measured in nitromethane solution have values in agreement with those reported in the literature for 1/1 electrolytes [22]. The analytical results and other data for the novel complexes are listed in Table 1.

The IR spectra show the absorptions of the uncoordinated anion PF_6^- (ca. 840, 560 cm^{-1}) along with characteristic bands of the coordinated diolefins. The carbonyl complex has two $\nu(CO)$ bands at 2101 and 2032 cm^{-1} (Fluorolube mull) which is in

TABLE 1

ANALYTICAL RESULTS, COLOUR, YIELDS, AND CONDUCTIVITIES (in CH_3NO_2) OF THE BORAZINERHODIUM(I) COMPLEXES I–VI

Complex	Colour	Yield (%)	Analysis (Found (calcd.) (%))			Λ_M ($cm^2\ \Omega^{-1}\ mol^{-1}$)
			C	H	Rh	
I	yellow	92	32.81	5.80	19.85	96
			(32.29)	(5.80)	(19.76)	
II	red-brown	89	30.51	4.82	20.60	100
			(30.94)	(5.19)	(20.39)	
III	pink	93	33.79	3.62	16.15	89
			(33.85)	(3.79)	(16.11)	
IV	yellow	95	37.83	4.13	15.70	102
			(37.05)	(4.44)	(15.12)	
V	orange	88	25.25	4.96	21.85	74
			(25.63)	(5.59)	(21.96)	
VI	brown	82	20.37	4.01	21.62	72
			(20.51)	(3.87)	(21.96)	

agreement with a *cis*-dicarbonyl structure. The spectra of all the complexes show a broad band in the 1370–1400 cm^{-1} region (Fluorolube mull), due to the stretching vibration ν(BN) of the coordinated hexamethylborazine and at lower wave numbers than the corresponding band for the free ring ligand [ν(BN) 1407 cm^{-1} (Fluorolube mull)]. For all the compounds the difference $\Delta\nu$(BN) between the stretching vibration of free and coordinated hexamethylborazine (see Table 2) is similar to that observed for neutral chromium compounds of the type $[Cr(CO)_3(R_3B_3N_3R'_3)]$ [8–11]. This is probably a result of lowering of the BN bond order of the borazine ring on complexation.

When KBr is used as solid support for the recording of the spectra only the ν(BN) band of free hexamethylborazine is observed, pointing to the occurrence of the following quantitative reaction in the solid state (eq. 3):

$$2[Rh(Me_3B_3N_3Me_3)(LL')]PF_6 + 2\ KBr \rightarrow [RhBr(LL')]_2 + 2\ Me_3B_3N_3Me_3 + 2\ KPF_6 \tag{3}$$

The ^1H NMR spectra in deuterated nitromethane or acetone solutions show resonances corresponding to the two types of methyl groups of uncoordinated hexamethylborazine at δ 0.50 (H_3CB) and 2.9 (H_3CN) ppm for all these complexes. No signals from the corresponding H_3CN and H_3CB protons of coordinated hexamethylborazine are observed. This indicates a high lability of the borazine rhodium complexes in these solutions, probably accompanied by the formation of solvate cationic species such as $[Rh(LL')S_x]^+$ through a rapid ring ligand displacement by the donor solvent molecules. The addition of an excess of hexamethylborazine to these solutions does not give the corresponding hexamethylborazine rhodium complexes. Similar observations were made with cationic complexes of general formula $[Rh(\eta^6\text{-arene})(Me_3TFB)]^+$ containing arenes of lower donor ability, such as benzene and naphthalene, as ligands [19,24].

When deuteriated dichloromethane is used two ^1H NMR signals in the ratio 1/1 are observed, corresponding to the B-CH_3 and N-CH_3 protons of the coordinated borazine ligand. This is in agreement with a hexahapto bonding to the metal. However, after a few minutes a rapid equilibrium is established in this solvent, as indicated by the appearance of the corresponding signals of the uncoordinated hexamethylborazine ligand (eq. 4):

$$[Rh(Me_3B_3N_3Me_3)(LL')]PF_6 + CD_2Cl_2 \rightleftharpoons [R(LL')(CD_2Cl_2)_x]PF_6 + Me_3B_3N_3Me_3 \tag{4}$$

This equilibrium can be shifted towards the right by dilution of the solution and to the left by addition of an excess of the hexamethylborazine ligand. In this case a broadening of the CH_3 signals is observed, indicating a rapid ring ligand exchange between free and coordinated hexamethylborazine. This equilibrium process was studied in some detail for complex I. In a saturated CD_2Cl_2 solution at room temperature (20°C) the ratio between free and coordinated hexamethylborazine is ~ 2/3 as indicated by the relative intensities of the corresponding H_3C-B signals. On going to 0, −40, then −50°C this ratio becomes progressively smaller, in agreement with the expectation that the equilibrium is displaced to the left at lower temperature. The opposite effect is observed when the temperature is raised above 20°C.

After standing, the solutions of the borazine rhodium complexes in CD_2Cl_2 decompose, to give products which have not been characterized. The compounds III and VI dissolve in CD_2Cl_2 at room temperature but there is rapid decomposition after a few minutes and free hexamethylborazine is formed. The most characteristic ^1H NMR data for the new complexes (in CD_2Cl_2) are summarized in Table 2.

In the ^1H NMR spectra of the complexes I, II, IV–VI the signal from the B-CH_3 groups is generally shifted towards lower fields ($\sim$ 0.3–0.45 ppm) relative to the signal of free hexamethylborazine. This indicates that the electron density at the boron atoms is greater in the coordinated than in the free hexamethylborazine. A similar phenomenon is observed for the signal from the N-CH_3 groups, which is also shifted towards lower fields ($\sim$ 0.1–0.25 ppm) on coordination. This observation suggests a high back donation from the rhodium to the boron atoms and a relative weak donor effect of the nitrogen atoms of the ring ligand. The opposite effect was observed with the chromium complex $[Cr(CO)_3(Me_3B_3N_3Me_3)]$ [8]. The greater lability of the rhodium compounds is probably the consequence of these bond properties.

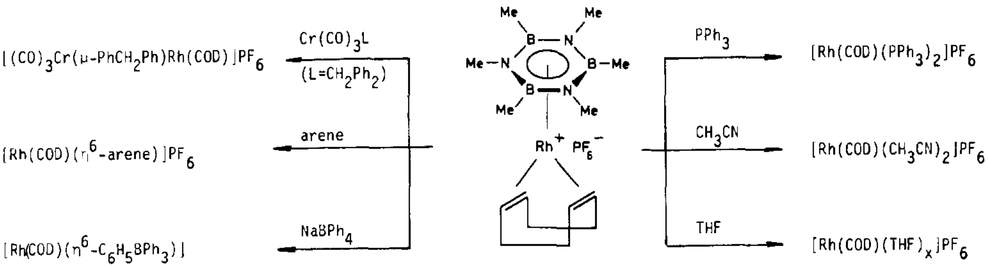
Some examples illustrating the high reactivity of the cyclooctadiene complex I are summarized in Scheme 1. The addition of N, P, or O donor ligands to a dichloromethane solution of the starting material results in a fast displacement of the coordinated hexamethylborazine accompanied by the formation of known products [17,25,26]. Furthermore, the use of the borazine rhodium compounds I–IV provides a new method of obtaining $[Rh(\eta^6\text{-arene})(LL')]^+$ cations [18] or neutral species such as $[Rh(COD)(\eta^6\text{-}C_6H_5BPh_3)]$. The naphthalene complex VII, which was previously unknown, can also be prepared by this route. The ^1H NMR spectrum of this compound (in CD_2Cl_2) shows two multiplets at δ 6.65 and 7.35 ppm for the coordinated naphthalene, compared with δ 7.48 (m) and 7.84 (m) ppm for free

TABLE 2

IR AND ^1H NMR DATA FOR THE HEXAMETHYLBORAZINE COMPLEXES I–VI (IR: in Fluorolube mull, ν in cm^{-1}; ^1H NMR: in CD_2Cl_2, δ in ppm, TMS int.)

Complex	IR		^1H NMR			
	ν(BN)	$\Delta\nu$(BN)	$\delta(BCH_3)$	$\delta(NCH_3)$	δ(L)	
I	1375	32	0.83	3.00	4.10	(=CH–)
					2.2	$(-CH_2-)$
II	1365	42	0.80	3.03	3.94	(=CH–)
					2.3	$(>CH-)$
					1.30	$(-CH_2-)$
III [a]	1370	37	0.50	2.90	4.0	(=CH–)
					5.8	$(>CH-)$
IV [b]	1390	17	0.88	3.08	2.36	$(\geq CCH_3)$
					1.58	$(=C(CH_3)-)$
V	1380	27	0.80	3.00	3.31	$(=CH_2)$
VI	1379	28	0.95	3.15	–	–

[a] The ^1H NMR signals correspond to free hexamethylborazine and the solvated species. [b] The signals of the CH protons of the Me_3TFB ligand are masked by the solvent.



(I)

SCHEME 1

$C_{10}H_8$. The signals of the COD protons are observed at δ 4.68 (m, CH) and 1.98 (m, CH_2) ppm.

Preliminary experiments indicate that compounds V and VI behave similarly to I, undergoing smooth ring ligand displacement upon addition of N and P donor or of arene ligands (e.g., benzene, mesitylene or hexamethylbenzene). On addition of naphthalene, displacement of the hexamethylborazine again takes place, to give products which could be observed only in solution. Attempts to isolate the PF_6 salts of these dicarbonyl and diethylenerhodium cations failed. At present we are trying to prepare the corresponding iridium complexes, which are thought to be more stable than their rhodium analogues.

Experimental

All reactions were carried out in Schlenk tubes under purified nitrogen and in the absence of light. Reagent grade solvents were dried and distilled before use. $RhCl_3 \cdot aq$, $[RhCl(CO)_2]_2$ and $[RhCl(C_2H_4)_2]_2$ were obtained from Strem Chemical Inc. $B_3N_3Me_6$, TFB and Me_3TFB were prepared by published procedures [28,29]. Infrared spectra were recorded on a Perkin-Elmer 567 spectrophotometer using Fluorolube mulls between KBr discs, or in CH_2Cl_2 solution between KBr plates. Conductivities were measured in ca. 5×10^{-4} *M* nitromethane or acetone solution with a Kuntze LMB-5 conductometer. ^1H NMR spectra were recorded on a Varian XL-100 instrument with TMS as reference.

Synthesis of the complexes $[Rh(Me_3B_3N_3Me_3)(diolefin)]PF_6$ (I–IV)

A slurry of ca. 1.0 mmol $[RhCl(diolefin)]_2$ (diolefin = COD [30], NBD [31], TFB of Me_3TFB [32]), the stoichiometric amount of $AgPF_6$, and a large molar excess of hexamethylborazine in 20 ml of CH_2Cl_2 was stirred for 30 min at room temperature. (In the case of TFB the reaction was carried out at −40°C). The precipitated AgCl was removed by filtration through kieselgur and the solution was evaporated to dryness. The excess of hexamethylborazine was extracted with n-hexane and after filtration the solid complex was washed with n-hexane and dried in vacuo.

Synthesis of the complexes $[Rh(Me_3B_3N_3Me_3)(C_2H_4)_2]PF_6$ (V) and $[Rh(Me_3B_3N_3Me_3)(CO)_2]PF_6$ (VI)

A suspension of ca. 1.0 mmol $[RhCl(C_2H_4)_2]_2$ or $[RhCl(CO)_2]_2$, respectively, in 20 ml dichloromethane was treated with the stoichiometric amount of $AgPF_6$ and a large excess of hexamethylborazine. After stirring for 60 min (V) or 30 min (VI) at low temperature (−40°) and filtration through kieselgur (to remove AgCl) the filtrate was evaporated to dryness. Addition of n-hexane produced an orange solid which was filtered off, repeatedly washed with n-hexane, and dried in vacuo.

Synthesis of $[Rh(C_{10}H_8)(COD)]PF_6$ *(VII)*

A suspension of 98.6 mg (0.2 mmol) $[RhCl(COD)]_2$ in 15 ml acetone was treated with 100 mg (0.78 mmol) naphthalene and 101.2 mg (0.4 mmol) $AgPF_6$. After 30 min stirring at room temperature and filtration through kieselgur, the pale-yellow filtrate was concentrated to a small volume and diethyl ether was added. A white microcrystalline solid was formed (150.0 mg; 78% yield). (Found: C, 44.19; H, 4.23; Rh, 21.37. $C_{18}H_{20}F_6PRh$ calcd.: C, 44.65; H, 4.16; Rh, 21.25%). Λ_M 116 $cm^2\ \Omega^{-1}\ mol^{-1}$ (in acetone).

Reactions of the complex $[Rh(Me_3B_3N_3Me_3)(COD)]PF_6$ *(I)*

(i) A dichloromethane solution of the hexamethylborazine complex I was treated with a slight excess of the corresponding arene ligand (C_6H_6, C_6Me_6). The mixture was stirred for 5 min and concentrated in vacuo. On addition of diethyl ether the arene complex separated and was characterized by the ^1H NMR spectrum [18]. The naphthalene complex VII and the binuclear compound $[(CO)_3Cr(\mu\text{-}C_6H_5CH_2\text{-}C_6H_5)Rh(COD)]PF_6$ were obtained similarly.

(ii) A dichloromethane solution of I was treated with PPh_3 and CH_3CN, and after stirring for 5 min the solvent was removed in vacuo. The product was recrystallized from CH_2Cl_2/ether and characterized by the IR and ^1H NMR spectra [25,26]. No well defined metal compound could be isolated after stirring a solution of complex I in THF [17]. Quantitative formation of free hexamethylborazine was revealed by ^1H NMR measurements.

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