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Synthetic and mechanistic studies on tripledecker complexes with bridging 1*H*-borole ligands

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Abstract

A mechanistic model for the nucleophilic degradation of tripledecker complexes like μ-(η^5-C_4H_4BPh)[Rh(η^5-C_4H_4BPh)]$_2$ is proposed. The rate-determining step is a lateral nucleophilic attack at one of the metal centres which is followed by fast addition of two further ligand molecules. The nucleophilic degradation of μ-(η^5-C_4H_4BPh)[Rh(η^5-C_4H_4BPh)]$_2$ by e.g. PMe_3, $P(OMe)_3$, $CNBu^t$ and NH_3 is reversible.

Stacking reactions, mainly by means of electrophilic addition to 1-phenylboratаferrocene ion, provide a strategy for the synthesis of new heterobimetallic tripledecker complexes including e.g. the group 5 compounds μ-(η^5-C_4H_4BPh)[M(CO)$_4$](FeCp) (M = V, Nb, Ta) and the group 6 anions [μ-(η^5-C_4H_4BPh)[M(CO)$_3$](FeCp)]$^-$ (M = Cr, Mo, W). In this context the electron count of tripledecker complexes is discussed. In the presence of strong σ-donor/π-acceptor ligands as outer ligands these complexes obey a strict 30e rule.

The combination of an electrophilic stacking reaction and a nucleophilic degradation reaction may result in a net ligand transfer. Examples demonstrate the transfer of borole ligands from Fe to Re, and from Co to Ru and Ir via tripledecker intermediates.

The 1*H*-borole ring system **1** is a 4π-electron system. MO considerations show that **1** possesses a diene-like HOMO and a low-lying LUMO which is essentially situated at the boron atom and to a lesser degree in the region between C-3 and C-4 of the ring. The low-lying LUMO dominates the fundamental properties of the borole ring:

(i) The borole ring system may act as a Lewis acid;
(ii) it may be reduced to form borole dianions [1];
(iii) it binds to transition metal centres as a strongly back-bonding ligand [2];

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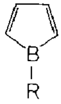
(iv) and, last but not least, it undergoes Diels–Alder dimerization unless it is sterically protected [3].



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In recent years we have shown that (η^5-borole)metal complexes can readily be made from dihydroboroles by means of a variety of synthetic methods [4]. We are now in a position to investigate the reactivity of these complexes in a systematic manner. In this contribution we wish to discuss:

(i) mechanistic aspects of the nucleophilic degradation of tripledecker complexes;

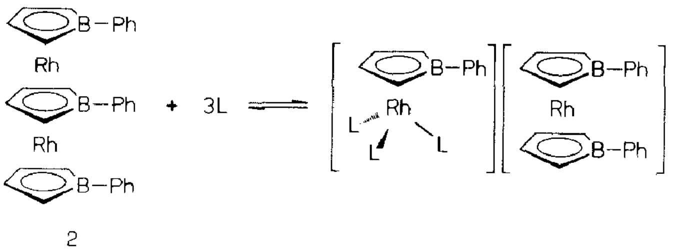
(ii) syntheses of new heterobimetallic tripledecker complexes with bridging borole ligands;

(iii) transfer of borole ligands from one metal to another via tripledecker intermediates.

Mechanistic aspects of the nucleophilic degradation of tripledecker complexes

The tripledecker complex μ-(η^5-C_4H_4BPh)[Rh(η^5-C_4H_4BPh)]$_2$ (**2**) is readily available from 1-phenyldihydroboroles and Cramer's complex [RhCl(η^2-C_2H_4)$_2$]$_2$ [5]. With a large variety of nucleophiles it undergoes nucleophilic degradation according to Scheme 1 [5].

Phosphorus ligands like PMe_3 and $P(OMe)_3$, with cone angles $\leqslant 136°$ (for $PMePh_2$), as well as t-butyl isocyanide smoothly react at room temperature in what appears to be quantitative reactions. Isolated yields amount to 85–95% [5]. A different situation is found for ammonia and primary amines [6]. When liquid ammonia is added to a THF solution of **2** a colour change from orange-red to light yellow is observed above $-30\,°C$. The ^1H NMR spectrum of this solution shows quantitative formation of the salt [Rh(NH_3)$_3$(η^5-C_4H_4BPh)][Rh(η^5-C_4H_4BPh)$_2$]. If after warming to ambient temperature the ammonia is allowed to escape, the nucleophilic degradation is reversed, and slow formation of **2** takes place. Thus, in the case of nitrogen nucleophiles, Scheme 1 describes an equilibrium which combines two important processes in the chemistry of tripledecker complexes: nucleophilic degradation of a tripledecker species, and electrophilic stacking of a sandwich molecule with formation of a tripledecker complex.



Scheme 1

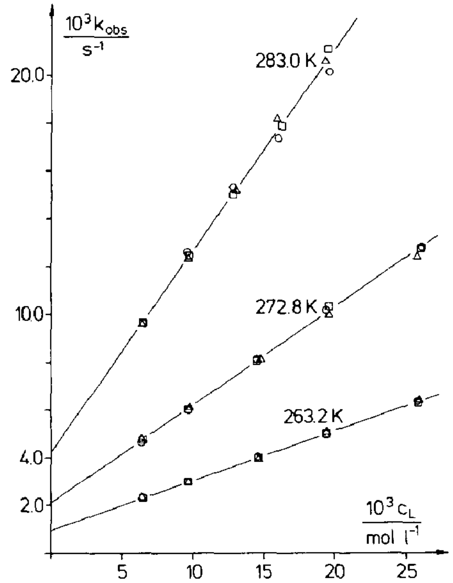


Fig. 1. Rate constants k_{obs} for the system **2**/PMe_3in CH_2Cl_2, as a function of ligand concentration c_L and temperature.

The nucleophilic degradation of **2** can be followed by means of photometry in the UV/Vis region of the spectrum. In the presence of a large excess of the attacking nucleophile L a pseudo first-order rate law and a linear dependence of the observed rate constants k_{obs} on the nucleophile concentration c_L is observed (Fig. 1) [6]. Thus, the tripledecker complex **2** is attacked by the nucleophile L in a bimolecular rate-determining step. The observation of an intercept cannot be interpreted in terms of a parallel first-order reaction which would be independent on the nature of the nucleophile L. It merely shows that even in the case of phosphines there is an equilibrium as mentioned above for ammonia and primary amines. The reverse reaction can also be observed directly. When crystalline $[Rh(PMe_3)_3(\eta^5\text{-}C_4H_4BPh)][Rh(\eta^5\text{-}C_4H_4BPh)_2]$ is dissolved in CH_2Cl_2 slow formation of **2** is observed until equilibrium is reached [6].

Table 1

Rate constants and activation parameters for the nucleophilic degradation of 2

L	T (K)	k (l mol^{-1} s^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J mol^{-1} K^{-1})
PMe_3	283.0	0.85(2)	41.5 ± 1.3	−99 ± 5
	272.8	0.407(5)		
	263.2	0.209(1)		
PEt_3	294.4	0.255(5)	53.5 ± 0.8	−74 ± 3
	283.1	0.100(5)		
	272.9	0.042(3)		
$P(OMe)_3$	293.4	0.150(6)	44.4 ± 1.3	−109 ± 5
	282.9	0.0763(4)		
	272.9	0.0355(5)		

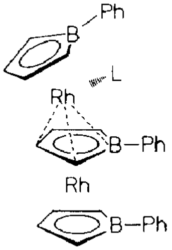
Table 2

Rate constants, $pK_A(LH^+)$ and cone angles for the nucleophiles L

L	k (283 K) ($l\ mol^{-1}\ s^{-1}$)	k_{rel}	pK_A [9]	θ (°) [8]
PMe_3	0.847	100	8.65	118
PEt_3	0.100	12	8.69	132
$P(OMe)_3$	0.076	9	2.60	107

Table 1 shows the low activation energies and the rather negative activation entropies [6] which are consistent with an associative process. Table 2 compares reaction rates with properties of the nucleophiles. Attack by PEt_3 is one order of magnitude slower than degradation by PMe_3, and the very bulky trialkylphosphines PPr^i_3 and $P(C_6H_{11})_3$ do not react at all at room temperature. As the basicity of the phosphine is essentially the same within this series these observations demonstrate a remarkably strong steric effect. There is also a clear electronic effect. $P(OMe)_3$ is less bulky than PMe_3, but also less nucleophilic because of its lower basicity, and the even less basic PCl_3 does not react at all. This evidence demonstrates the nucleophilic character of the degradation.

We propose an associative mechanism. The rate-determining step is thought to be a lateral nucleophilic attack at one of the metal centres with concomitant slippage from η^5- to η^3-bonding which produces an intermediate **3** with a half-opened structure. The primary attack is then followed by fast addition of two further ligand molecules.



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Our mechanistic model is supported by observations in closely related systems. In μ-(η^5-C_4H_4BMe)[Co(η^5-C_4H_4BMe)]$_2$ the bond between the metal and the bridging ligand is longer and hence weaker than the bond to the outer ligands [7]. In 30e tripledecker compounds where, in contrast to **2**, inner and outer ligands are different, it is unambiguous that nucleophilic degradation breaks the bond between the metal and the bridging ligand (see examples below). The alternative of a primary nucleophilic attack at the *exo*-face of an outer borole ligand is unlikely as it could not explain the steric inhibition we observe for e.g. secondary amines. Secondary amines, which in contrast to NH_3 and $EtNH_2$ do not react with **2** [6], readily add to the *exo*-face of monofacially bound ring ligands as e.g. in $[(C_6H_7)Fe(CO)_3]^+$ [8] and many other systems [9].

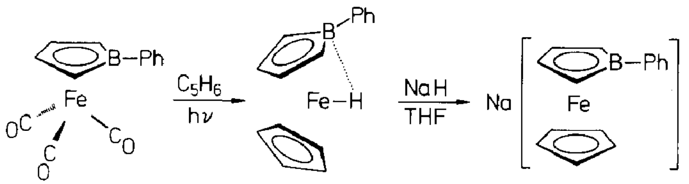
Previous examples for nucleophilic degradation of tripledecker complexes are the reactions of $[\mu\text{-Cp}\{NiCp\}_2]^+$ with Lewis bases [10], and the cyclopentadienide degradation of tripledecker compounds with bridging dihydro-1,2,5-thiadiborole, $(EtC)_2(BMe)_2S$ [11], borole [5,7] and benzene ligands [12].

Syntheses of new heterobimetallic tripledecker complexes

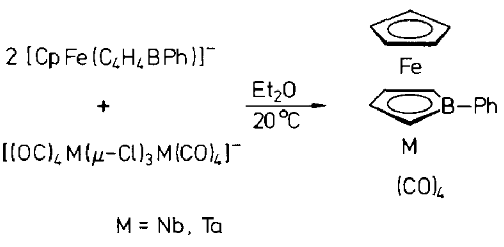
If the nucleophilic degradation is reversed, an electrophilic stacking reaction takes place. This notion provides a general synthetic strategy for the preparation of new tripledecker complexes. The necessary closed-shell sandwich anions are most readily available via nucleophilic degradation of tripledecker compounds, but the less common case where the anion can be obtained via alternative routes is by far more useful. Scheme 2 gives an example for such a situation.

Exhaustive photochemical decarbonylation of tricarbonyl[η^5-(1-phenylborole)]-iron in the presence of cyclopentadiene provides the hydride $CpFeH((\eta^5\text{-}C_4H_4BPh)$ which upon treatment with NaH in THF gives the sodium salt of the 1-phenylborataferrocene ion [13]. Electrophilic stacking of the anion with $M(CO)_3$ fragments (M = Cr, Mo, W) produces the heterobimetallic anion $[\mu\text{-}(\eta^5\text{-}C_4H_4BPh)\{M(CO)_3\}\text{-}(FeCp)]^-$ (M = Cr) [14] and its higher homologues (M = Mo, W) [15]. The reaction with group 5 carbonylmetal compounds $[(\mu\text{-}Cl)_3\{M(CO)_4\}_2]^-$ (M = Nb, Ta) [16] yields the tripledecker complexes $\mu\text{-}(\eta^5\text{-}C_4H_4BPh)[M(CO)_4](FeCp)$ (M = Nb, Ta) [17] as shown in Scheme 3; these complexes constitute the first tripledecker species of niobium and tantalum. We emphasize that the new tripledecker species described here all are 30e systems.

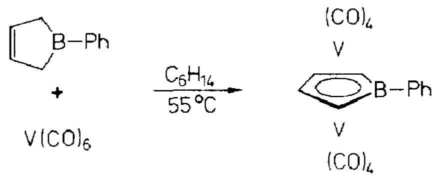
In the case of vanadium a different method had to be developed. The hydride $CpFeH(\eta^5\text{-}C_4H_4BPh)$ slowly reacts with $V(CO)_6$ at room temperature to form the vanadium analogue $\mu\text{-}(\eta^5\text{-}C_4H_4BPh)[V(CO)_4](FeCp)$. In this context we also mention the formation of the related vanadium complex $\mu\text{-}(\eta^5\text{-}C_4H_4BPh)[M(CO)_4]_2$ from $V(CO)_6$ and 1-phenyl-2,5-dihydroborole (Scheme 4) [17]. These two compounds are the first 30e tripledecker complexes of vanadium while the two known types $\mu\text{-}(\eta^6\text{-}C_6H_6)(VCp)_2$ [18] and $\mu\text{-}(\eta^6\text{-}P_6)[V(h^5\text{-}C_5Me_5)]_2$ [19] possess 26e configuration.



Scheme 2



Scheme 3



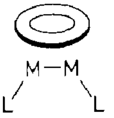
Scheme 4

There has been considerable discussion related to the electron count of tripledecker complexes. In a now classical paper Hoffmann et al. have shown that tripledecker complexes with 30 and 34 electrons should have closed-shell configurations [20]; this result has often been quoted as the 30/34e rule. Application of the cluster rules [21] gives a magic number of 30 electrons. Yet the electron count of the known isolated tripledecker complexes [22] varies from 26 for μ-(η^6-C_6H_6)(VCp)$_2$ [18] to 34 for [μ-Cp(NiCp)$_2$]$^+$ [7,23,24].

This apparent discrepancy should not be too surprising. The situation here is much the same as with the 18e rule. While the 18e rule is strong for binary carbonyls it is a weak rule for metallocenes, especially of the 3*d* metals. In the presence of strong σ-donor/π-acceptor ligands such as CO the lower *d* orbitals (corresponding to t_{2g} in octahedral symmetry) are strongly bonding orbitals and the higher *d* orbitals (corresponding to e_g in octahedral symmetry) are strongly antibonding; thus the electron count must be precise. On the other hand, when all *d* orbitals are closer to a non-bonding situation, deviations from the magic count are more likely; this situation is found in e.g. VCp$_2$ and NiCp$_2$ as well as in tripledecker complexes with outer cyclopentadienyl ligands such as μ-(η^6-C_6H_6)(VCp)$_2$ and [μ-Cp(NiCp)$_2$]$^+$. We conclude: tripledecker complexes with strong σ-donor/π-acceptor ligands as outer ligands obey a strict 30e rule.

Transfer of borole ligands from one metal to another via tripledecker intermediates

The principle and the preparative value of ring ligand transfer reactions [25] have first been demonstrated for (cyclobutadiene)metal complexes [26,27]. These reactions were thought to proceed via binuclear intermediates **4** where the ligand transferred is monofacially bound in a bridging position between the two metal centres [27]. This hypothesis gained strength when stable binuclear complexes [24] such as μ-(η^6-C_6H_6)$_2$[Pd(Al_2Cl_7)]$_2$(*Pd–Pd*) [28] with monofacially bound, bridging ring ligands were discovered and structurally characterized [28].



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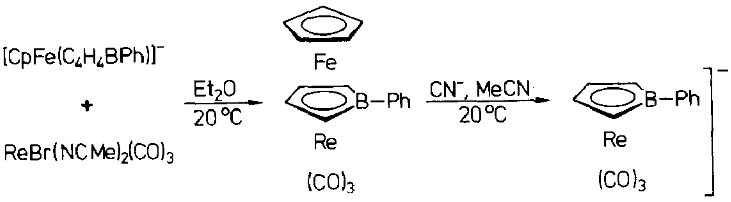
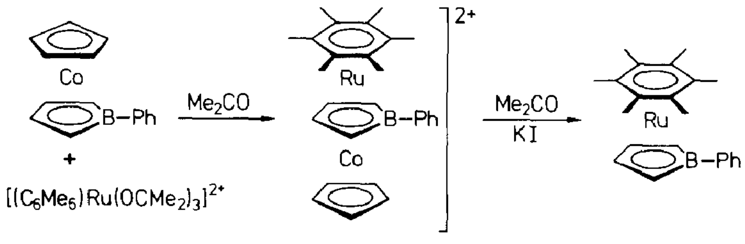
In the case of heterobimetallic tripledecker complexes the combination of an electrophilic stacking reaction and a nucleophilic degradation reaction may result in a net ligand transfer. Scheme 5 shows the reaction of the 1-phenylborataferrocene ion with ReBr(CO)$_3$(NCMe)$_2$ which affords the stable purple heterobimetallic tripledecker complex μ-(η^5-C_4H_4BPh)(FeCp)[Re(CO)$_3$] [29]. Subsequent nucleophil-


Scheme 5

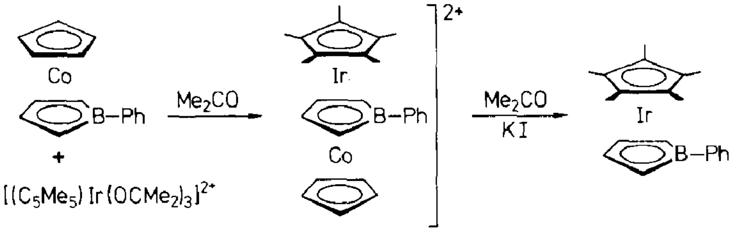

Scheme 6

ic degradation with NaCN in acetonitrile produces the colourless rhenate $[(\eta^5\text{-}C_4H_4\text{-}BPh)Re(CO)_3]^-$ which can be isolated and characterized as $[NMe_4]^+$ salt or after protonation as hydride $(\eta^5\text{-}C_4H_4BPh)ReH(CO)_3$ [29]. The reaction sequence is synthetically useful; it seems unlikely that more conventional synthetic methods would give these mononuclear rhenium complexes with similar efficiency.

Even the uncharged cobalt complex $CpCo(\eta^5\text{-}C_4H_4BPh)$ which is isoelectronic to the 1-phenylborataferrocene ion is amenable to electrophilic stacking reactions (Scheme 6). With the salt $[(\eta^6\text{-}C_6Me_6)Ru(acetone)_3](BF_4)_2$, generated in acetone, the sensitive, reddish brown salt $[\mu\text{-}(\eta^5\text{-}C_4H_4BPh)(CoCp)\{Ru(\eta^6\text{-}C_6Me_6)\}](BF_4)_2$ is formed [29]. Addition of KI effects degradation to the known sandwich complex $(\eta^6\text{-}C_6Me_6)Ru(\eta^5\text{-}C_4H_4BPh)$ [30].

In a similar stacking reaction with $[(\eta^5\text{-}C_5Me_5)Ir(acetone)_3]^{2+}$ the labile cation $[\mu\text{-}(\eta^5\text{-}C_4H_4BPh)(CoCp)\{Ir(\eta^5\text{-}C_5Me_5)\}]^{2+}$ can be observed in the NMR tube (Scheme 7). However, the degradation product $(\eta^5\text{-}C_5Me_5)Ir(\eta^5\text{-}C_4H_4PBh)$ appears in the reaction mixture before the stacking reaction is complete [29].

The reactions discussed here provide a simple, new mechanistic model for ring ligand transfer reactions. By way of extrapolation situations can be envisaged where the degradation step is faster than the stacking step. In such a case only the overall ring ligand transfer reaction would be observable. This mechanistic model implies stereospecificity of the ring ligand transfer. We are presently trying to verify this stereospecificity using complexes of prochiral borole derivatives.


Scheme 7

Very little mechanistic information is available on the related ring ligand transfer reactions of cyclobutadiene, cyclopentadiene, boratabenzene [30], and benzene complexes. We suggest that there also ring ligand transfer via tripledecker intermediates should be considered as a mechanistic possibility.

Acknowledgement

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