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REACTIONS OF 1,4-DIAZA-3-METHYLBUTADIEN-2-YLPALLADIUM(II) DERIVATIVES WITH CHLORO-BRIDGED RHODIUM(I) COMPLEXES

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Summary

The reactions of the organometallic 1,4-diazabutadienes, RN=C(R′)C(Me)=NR″ [R = R″ = p-C_6H_4OMe, R′ = *trans*-$PdCl(PPh_3)_2$ (DAB); R = p-C_6H_4OMe, R″ = Me, R′ = *trans*-$PdCl(PPh_3)_2$ (DAB^I); R = R″ = p-C_6H_4OMe, R′ = Pd(dmtc)-(PPh_3), dmtc = dimethyldithiocarbamate (DAB^{II}); R = R″ = p-C_6H_4OMe, R′ = PdCl(diphos), diphos = 1,2-bis(diphenylphosphino)ethane (DAB^{III})] with $[RhCl(COD)]_2$ (COD = 1,5-cyclooctadiene, Pd/Rh ratio = 1/2) depend on the nature of the ancillary ligands at the Pd atom in group R′. In the reactions with DAB and DAB^I transfer of one PPh_3 ligand from Pd to Rh occurs yielding [RhCl(COD)(PPh_3)] and the new binuclear complexes [Rh(COD){RN=C(R‴)-C(Me)=NR″}], in which the diazabutadiene moiety acts as a chelating bidentate ligand. Exchange of ligands between the two different metallic centers also occurs in the reaction with DAB^{II}. In this case, the migration of the bidentate dmtc anion yields [Rh(COD)(dmtc)] and [Rh(COD){RN=C(R‴)C(Me)=NR″}]. In contrast, the reaction with DAB^{III} leads to the ionic product [Rh(COD)-(DAB^{III})][$RhCl_2$(COD)], with no transfer of ligands. The cationic complex $[Rh(COD)(DAB^{III})]^+$ can be isolated as the perchlorate salt from the same reaction (Pd/Rh ratio = 1/1) in the presence of an excess of $NaClO_4$. In all the binuclear complexes the coordinated 1,5-cyclooctadiene can be readily displaced by carbon monoxide to give the corresponding dicarbonyl derivatives. The reaction of $[RhCl(CO)_2]_2$ with DAB and/or DAB^I yields trinuclear complexes of the type $[RhCl(CO)_2]_2$(DAB), in which the diazabutadiene group acts as a bridging bidentate ligand. Some reactions of the organic diazabutadiene RN=C(Me)C(Me)=NR (R = p-C_6H_4OMe) are also reported for comparison.

TABLE 1

ANALYTICAL AND PHYSICAL DATA

Compound	Colour	Melting point (°C) [a]	C [b] (%)	H (%)	N (%)	Cl (%)	Molecular weight [b]	Λ_M (ohm^{-1} cm^2 mol^{-2}) [c]
Ia	Dark-green	178	55.2	4.8	2.9	7.6	938	
			(55.41)	(4.76)	(3.01)	(7.61)	(932)	
Ib	Green	187	52.0	4.7	3.3	8.6	826	
			(52.90)	(4.80)	(3.33)	(8.44)	(840)	
IIa	Red	198	50.1	3.8	3.1	8.1	940	
			(50.51)	(3.67)	(3.18)	(8.06)	(879.8)	
IIb	Yellow-orange	200	47.2	3.7	3.5	8.9		
			(47.26)	(3.58)	(3.56)	(9.00)		
IIIa	Dark-green	228	53.9	4.9	2.4	6.5		79.7
			(54.10)	(4.71)	(2.47)	(6.26)		
IIIb	Dark-green	225—234	52.1	5.4	4.6	6.0		87.3
			(51.45)	(5.31)	(4.61)	(5.84)		
IVa	Dark-blue	189	49.5	4.0	2.5	6.7		77.8
			(50.04)	(3.83)	(2.59)	(6.56)		
IVb	Dark-brown	200	42.8	3.7	4.9	6.5		91.3
			(43.30)	(3.63)	(5.05)	(5.39)		
Va	Red	168	51.0	3.7	2.0	8.0	1036 [d]	
			(51.22)	(3.54)	(2.09)	(7.95)	(1336.5)	
Vb	Red-orange	167	49.3	3.6	2.2	8.6	1016 [e]	
			(49.22)	(3.48)	(2.25)	(8.54)	(1244.4)	

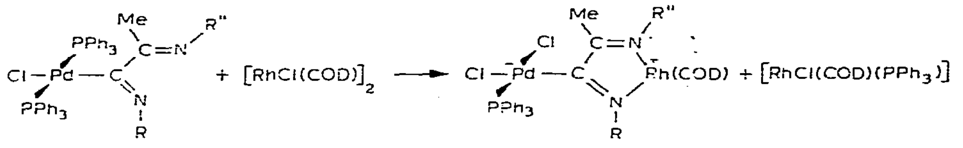
[a] Uncorrected values: all compounds decompose on melting. [b] The calculated values are reported in parenthesis. [c] The conductivity measurements have been carried out on MeOH solutions 10^{-3} *M* at 20°C. [d] Experimental molecular weight for a solution 3.53×10^{-3} *M*. A value of 951 was found for a solution 1.98×10^{-3} *M*. [e] Experimental molecular weight for a solution 4.01×10^{-3} *M*. A value fo 990 was found for a solution 2.26×10^{-3} *M*.

Introduction

In previous papers we described the preparation of organometallic derivatives of palladium(II) containing a σ-bonded 1,4-diaza-3-methylbutadien-2-yl-group * [1—5]. The compounds RN=(R')C(Me)=NR" may either (a) have the same substituents on both imino N atoms (R = R" = Ph, p-C_6H_4Me, p-C_6H_4OMe, C_6H_{11}) with different ligands and configurations at the Pd atom of the group R' [R' = *trans*-$PdCl(PPh_3)_2$, PdCl(diphos), $Pd(dmtc)(PPh_3)$; diphos = 1,2-bis(diphenylphosphino)ethane, dmtc = dimethyldithiocarbamate], or (b) have different substituents on the two imino N atoms (R = p-C_6H_4OMe, C_6H_{11} and R" = Me, p-C_6H_4OMe, respectively) with the same group R' [R' = *trans*-$PdCl(PPh_3)_2$]. We have also found that the diazabutadiene moiety acts as a chelating bidentate ligand towards metal ions of the first transition series to give the binuclear complexes $[MX_2\{RN=C(R')C(Me)=NR''\}]$ (M = Fe, Co, Ni, Cu, Zn; X = Cl, Br) [3,4]. Studies on the coordinating abilities of this new type of ligands have recently been extended to metal ions of the later transition series [5]. In this context, we report here some reactions of the organometallic diazabutadienes with chloro-bridged dimeric rhodium(I) complexes.

Results and discussion

The organometallic α-diimines RN=C(R')C(Me)=NR" [R' = *trans*-$PdCl(PPh_3)_2$] react very rapidly with $[RhCl(COD)]_2$ (COD = 1,5-cyclooctadiene) as shown in eqn. 1. In this reaction one PPh_3 ligand migrates from DAB and/or DAB^I to a Rh center of the dimer $[RhCl(COD)]_2$ yielding the complex $[RhCl(COD)(PPh_3)]$, which can be isolated and identified by elemental analysis and by IR and ^1H NMR spectra [6]. A Pd/Rh ratio of 1/2 is required to drive the reaction to completion. When a Pd/Rh ratio of 1/1 is used, only 50% of the starting diazabutadiene ligand reacts, according to eqn. 1, and the remaining 50% is left unchanged.



(1)

R = R" = p-C_6H_4OMe (DAB) (Ia)

R = p-C_6H_4OMe, R" = Me (DAB^I) (Ib)

The binuclear complexes I are non-conducting monomeric compounds (Table 1). The formulation of I is mainly based on spectral data and chemical reactions. The coordination of COD to rhodium(I) is indicated by reactions 2 and 3 with PPh_3 and CO.

In reaction 2 the Rh(COD) unit is completely displaced from the diazabutadiene moiety to give the complex $[RhCl(COD)(PPh_3)]$. One PPh_3 molecule reacts also at the Pd atom yielding DAB and/or DAB^I (i.e., the starting materials

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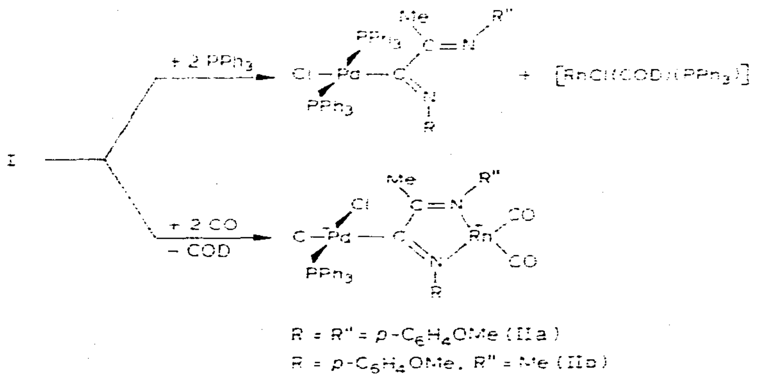
* Alternative nomenclature: 1,2-bis(imino)propyl group [3].



(2)

(3)

of reaction 1). In reaction 3, the coordinated COD is quantitatively displaced by carbon monoxide to give the dicarbonyl derivatives II—a typical reaction of the cationic complexes [Rh(COD)(L—L)]$^+$ (L—L = chelating bidentate N-donor ligand) [7].

Two strong ν(CO) bands are observed in the range 2100—2027 cm^{-1} for the dicarbonyl compounds II. All the binuclear complexes I and II are characterized by two metal—chloride stretching vibrations in the range 308—276 cm^{-1}, which are assigned to ν(PdCl) bands of two mutually *cis* chlorides in *trans* position to

TABLE 2

CHARACTERISTIC IR BANDS (cm^{-1})[a]

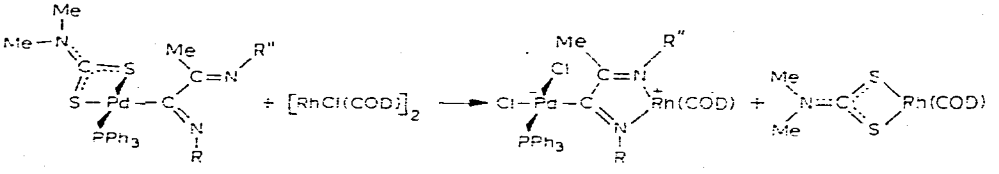
Compound	ν(CO)	ν(CN)[b]	ν(MCl)[c]	Other bands	
Ia		1605s or 1584m; 1526m	299s; 276ms		
Ib		1604ms or 1587w; 1521m	308ms; 285ms		
IIa	2086s; 2027s (2095s; 2038s)	1604s or 1582m; 1515(sh)	306m; 285m		
IIb	2087; 2038s[d]	1602ms or 1583m; 1510(sh)	298m; 276m		
IIIa		1605ms or 1586m; 1520(sh)	304m	1090s(br) 621s	ν(ClO) δ(ClO)
IIIb		1608s or 1583m		1090s(br) 625s	ν(ClO) δ(ClO)
IVa	2091s; 2037s (2097s; 2040s)	1605ms or 1584m; 1510(sh)	296m	1095s(br) 624s	ν(ClO) δ(ClO)
IVb	2096s; 2047s (2100s; 2045s)	1607s or 1583m		1100s(br) 626s	ν(ClO) δ(ClO)
Va	2100s; 2066s 2040s; 1986s (2100s; 2073s; 2044s; 1992s)	1601ms or 1583m	320m; 304m; 295m		
Vb	2090s; 2061s; 2032s; 1978s (2095s; 2072s; 2038s; 1992s)	1600ms or 1585m; 1510(sh)	327m; 302ms		

[a] The figures in parenthesis refer to CH$_2$Cl$_2$ solutions. [b] Tentative assignment because of the intense absorptions of the *para*-substituted phenyl rings around 1600 and 1500 cm^{-1}. [c] M = Pd and/or Rh. [d] Another weak ν(CO) band is present at 1985 cm^{-1}.

ligands of high *trans* influence, such as PPh_3 and the σ bonded 1,4-diaza-3-methylbutadien-2-yl group [3—5] (Table 2).

The presence of a chelating diazabutadiene group in I and II is also supported by the appearance of characteristic CT bands in the electronic spectra, as will be discussed later.

A fast migration of ligands also occurs in the reaction with RN=C(R')C(Me)=NR" [R' = Pd(dmtc)(PPh_3)] (4).



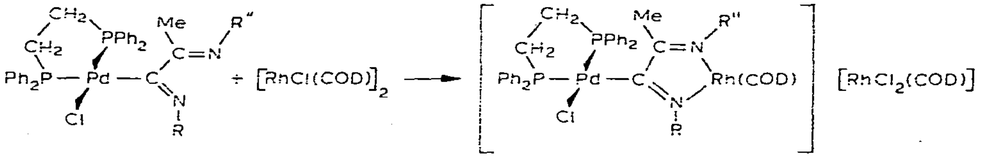
(4)

R = R" = p-C_6H_4OMe (DAB^{II})

(Ia)

The product Ia can be isolated and characterized as previously described. The complex [Rh(COD)(dmtc)] cannot be separated analytically pure, but its formation is confirmed by comparison of the ^1H NMR spectrum of the reaction mixture in $CDCl_3$, with that of an authentic sample independently prepared (see Experimental).

In contrast to DAB, DAB^I and DAB^{II}, the diazabutadiene RN=C(R')C(Me)=NR" [R' = PdCl(diphos)] reacts with $[RhCl(COD)]_2$ with no exchange of ligands between the different metal centers (5).



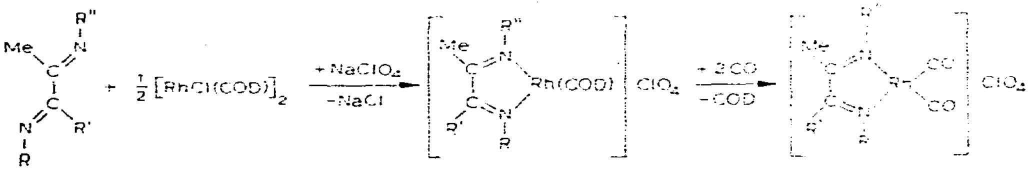
(5)

R = R" = p-C_6H_4OMe (DAB^{III})

The ionic product of this reaction cannot be isolated pure even after repeated precipitations from a variety of solvents. However, it can be characterized in the clear dark-green solutions resulting from the reactions in MeOH and $CDCl_3$ by conductivity measurements and ^1H NMR spectroscopy respectively. In particular the ^1H NMR spectrum of the reaction mixture in $CDCl_3$ is a superposition of the individual spectra of the anionic and cationic complexes independently prepared (see Experimental). The anion $[RhCl_2(COD)]^-$ is characterized by the signal of the equivalent olefinic protons at 4.15 ppm, whereas in the cation $[Rh(COD)(DAB^{III})]^+$ the same signal appears as an unresolved multiplet in the range 3.7—3.4 ppm, the integration ratio of the two peaks being ~1/1. A similar ionic compound, [Rh(COD)(bipy)][$RhCl_2$(COD)] (bipy = 2,2'-bipyridine), was obtained from the reaction of $[RhCl(COD)]_2$ with bipy [8].

The cationic complex [Rh(COD)(DAB^{III})]ClO_4 (IIIa) can be prepared in good yield from reaction (6).

As can be seen, the organometallic ligand DAB^{III} exhibits the same reactions as the organic diazabutadiene DAB^{IV}. All the complexes III and IV are uni-univalent electrolytes in MeOH solution. The presence of two mutually *cis* CO ligands in IV is confirmed by IR spectra (in the solid and in solution) and by



(6)

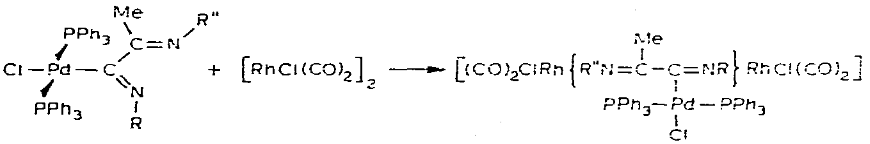
R = R'' = p-C_6H_4OMe
R' = PdCl(diphos)(DAB^{III})
R' = Me(DAB^{IV})

(IIIa)
(IIIb)

(IVa)
(IVb)

measurements of the volume of gas evolved upon treatment with an excess of diphos [9].

The reaction of DAB and/or DAB^I with $[RhCl(CO)_2]_2$ is reported in eqn. 7.



(7)

R = R'' = p-C_6H_4OMe
R = p-C_6H_4OMe; R'' = Me

(Va)
(Vb)

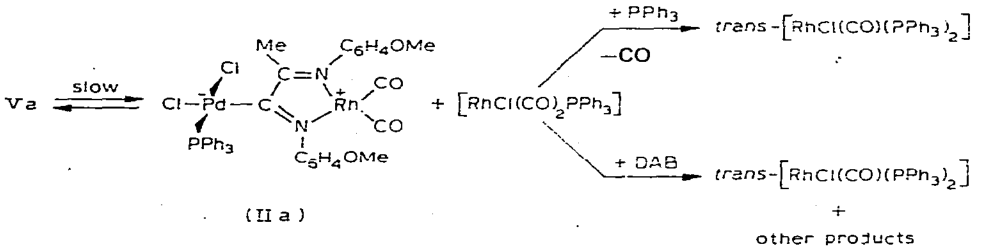
At variance with reactions 1, 4 and 5, this reaction yield the trinuclear complexes V, in which the 1,4-diaza-3-methylbutadien-2-yl group acts as a bidentate bridging ligand on two Rh(I) centers. The IR and ^1H NMR spectra of the reaction mixture in CH_2Cl_2 or $CDCl_3$, indicate a very fast and quantitative formation of V when a Pd/Rh ratio of 1/2 is used. The IR spectra of V in the solid and in solution show four intense $\nu(CO)$ bands in the range 2100—1978 cm^{-1}, due to two $RhCl(CO)_2$ units with *cis* CO ligands.

Although in the far IR region the $\nu(PdCl)$ and $\nu(RhCl)$ bands cannot be distinguished from each other, the $\nu(MCl)$ vibrations are found at significantly higher frequencies, 327—295 cm^{-1}, than $\nu(PdCl)$ of the free ligands (265 and 255 cm^{-1} for DAB and DAB^I, respectively [1,4]) and $\nu(Rh{-}Cl_{bridging})$ of $[RhCl(CO)_2]_2$ (284; 274 cm^{-1} [10]), owing to the reduced *trans* influence of the σ bonded 1,4-diaza-3-methylbutadien-2-yl group upon coordination [3,4] and to the splitting of chloro-bridges of the dimeric rhodium(I) complex [10].

The structure of V has not been determined by an X-ray analysis. However, from the ^1H NMR spectra it appears that the coordinated 1,4-diazabutadiene group is present in solution in only one of the possible configurations, probably that involving the least steric hindrance, with the C=N bonds in *trans* position.

Related polynuclear complexes with bridging bis(imino) ligands have been obtained in the reactions of $[RhCl(CO)_2]_2$ with the organic diazabutadiene t-BuN=CHCH=NBu-t [11] and with the organometallic compounds $[Hg\{C(=N\text{-}p\text{-}C_6H_4Me)OEt\}_2]$ and $[Pt\{C(=N\text{-}p\text{-}C_6H_4Me)OMe\}_2(diphos)]$, containing two mono-imino groups σ bonded to the central metal [12,13].

The complexes V are non-conducting in methanol and slightly dissociated in 1,2-dichloroetane solutions. The complex Va reacts relatively slowly (ca. 90 min for completion) with an equimolar amount of PPh_3 to give the well-known derivative *trans*-$[RhCl(CO)(PPh_3)_2]$ and the compound IIa, identified in solution on the basis of its IR and ^1H NMR spectra. On the other hand, when DAB is treated with $[RhCl(CO)_2]_2$ (Pd/Rh ratio 1/1), only 50% of the diazabutadiene ligand reacts immediately according to eqn. 7. On standing, a subsequent slower reaction takes place between Va and the unreacted DAB, yielding the complex IIa as the major product, and a mixture of minor derivatives among which *trans*-$[RhCl(CO)(PPh_3)_2]$ is again detected. This behaviour may be accounted for by the following series of reactions (8), where the initial step is assumed to be a slow dissociation of the trinuclear complex Va to IIa and the labile species $[RhCl(CO)_2(PPh_3)]$ *.



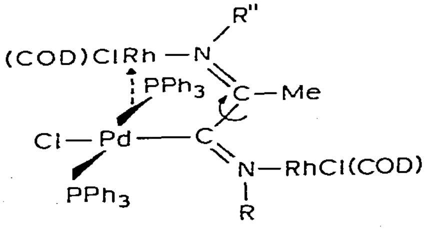
(8a)

(8b)

The binuclear complex $[(CO)_2ClRh\{t\text{-}BuN{=}CHCH{=}NBu\text{-}t\}RhCl(CO)_2]$ was reported to react with an equimolar amount of PPh_3 to yield $[\{t\text{-}BuN{=}CHCH{=}NBu\text{-}t\}RhCl(CO)_2]$ and the known compound $[RhCl(CO)_2(PPh_3)]$, i.e., a species containing only one PPh_3 molecule per Rh atom [11].

The slow dissociation of Va to IIa is confirmed by the ^1H NMR spectra of a pure sample of Va in $CDCl_3$ at various times, as shown in Fig. 1. The spectra (a) and (b) were recorded 10 min and 2 h. after dissolution of Va. The stronger singlet at 2.42 ppm is due to the 3-methyl group of the coordinated 1,4-diaza-3-methylbutadien-2-yl moiety of Va, while the weak but diagnostic singal at 2.96 ppm is due to the corresponding 3-methyl group of IIa. The relative intensity of the two peaks varies slowly with time until after ca. 2 h no appreciable change is observed. At this point, the integration gives a molar ratio IIa/Va ~ 1/10. The spectrum (c) is reported for comparison, and refers to an equimolar mixture of Va and PPh_3 when reaction 8a is completed.

The reactions of the trinuclear complex Va, and the dependence of reactions and 7 on the molar ratio of the reactants suggest a mechanism for reaction 1 involving a rapid formation of labile intermediated of the type V, which would decay to the final products with an intramolecular migration of ligands:



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* This compound was detected only in solution, where it undergoes reversible dimerisation to chloro-bridged derivatives [14].

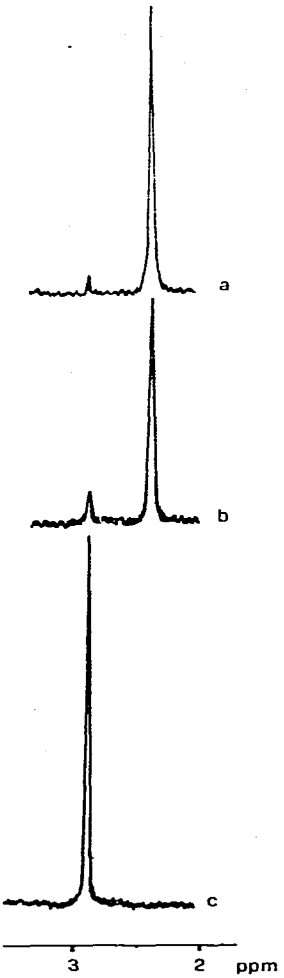

Fig. 1. ^1H NMR spectra in the range 3.5—2.0 ppm. (a) Compound Va 10 min after dissolution; (b) compound Va 2 h after dissolution; (c) equimolar mixture Va/PPh_3 when reaction 8a is completed.

The transfer of PPh_3 from Pd to Rh coordinated to the nitrogen atom at position 4 on the diazabutadiene chain would produce the compound [RhCl(COD)-(PPh_3)], and the resulting fragment would rearrange to the final products I by chelation to Rh coordinated to nitrogen at position 1.

The nature of the products of reaction 7 rules out an alternative mechanism based on a preliminary dissociation of DAB and/or DAB^I with release of free PPh_3, which would react with the dimer $[RhCl(COD)]_2$ to give [RhCl(COD)-(PPh_3)]. Dissociations of this type have been reported for the complexes *trans*-$[PdCl(CH_2C_6H_4Y)(PPh_3)_2]$ (Y = H, *o*-CN, *m*-CN, *p*-CN) containing a σ bonded benzyl group [15].

The rhodium(I) complexes I—V are generally moderately stable compounds either in the solid or in the solvents used for their preparation and characterization. Only the dicarbonyl derivative IIb cannot be studied in solution because

TABLE 3

^{1}H NMR SPECTRA [a]

Compound	Signal	Assignment
Ia	1.2—2.6 m, br	—CH_2—
	2.77 s	C—Me
	3.3—3.6 m	—CH=
	3.78 s	O—Me
	3.87 s	O—Me
	6.6—7.0 m	—C_6H_4—
	7.0—7.8 m	PPh_3 + —C_6H_4—
Ib	1.4—2.7 m, br	—CH_2—
	2.75 s	C—Me
	2.96 s	N—Me
	3.5—3.9 m	—CH=
	3.82 s	O—Me
	6.5—7.8 m	PPh_3 + —C_6H_4—
IIa	2.96 s	C—Me
	3.82 s	O—Me
	3.91 s	O—Me
	6.6—7.0 m	—C_6H_4—
	7.0—7.9 m	PPh_3 + —C_6H_4—
IIIa	1.0—3.1 m, br	—CH_2— + P—CH_2—
	2.13 s	C—Me
	3.4—3.7 m	—CH=
	3.78 s	O—Me
	3.80 s	O—Me
	6.3—8.0 m	—PPh_2 + —C_6H_4—
IIIb	1.5—2.6 m, br	—CH_2—
	2.12 s	C—Me
	3.77 s	O—Me
	3.7—3.9 m	—CH=
	6.7—7.2 m	—C_6H_4—
IVa	2.37 s	C—Me
	2.2—3.3 m, br	P—CH_2—
	3.81 s	O—Me
	3.84 s	O—Me
	6.5—8.2 m	—PPh_2 + —C_6H_4—
IVb	2.38 s	C—Me
	3.81 s	O—Me
	6.7—7.4 m	—C_6H_4—
Va	2.42 s	C—Me
	3.82 s	O—Me
	3.88 s	O—Me
	6.4—7.1 m	—C_6H_4—
	7.1—7.8 m	PPh_3 + —C_6H_4—
Vb	2.64 s	C—Me
	3.21 s	N—Me
	3.88 s	O—Me
	6.5—7.2 m	—C_6H_4—
	7.2—7.8 m	PPh_3
[Rh(dmtc)(COD)]	1.7—2.6 m	—CH_2—
	3.23 s	N—Me
	4.4 m	—CH=
[$RhCl_2$(COD)]$AsPh_4$	1.5—2.5 m	—CH_2—
	4.15 m	—CH=
	7.4—7.9 m	$AsPh_4$

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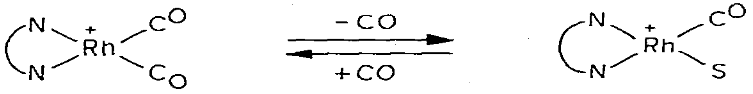
[a] Spectra recorded in $CDCl_3$ solution; δ values in ppm from TMS as internal standard; s singlet, m multiplet, br broad.

it decomposes rather quickly with loss of carbon monoxide.

The dicarbonyl complexes IIa, IVa and IVb do not dissociate with release of carbon monoxide in halogenated solvents even when dinitrogen is bubbled through the solution for a long time. However, upon addition of a small amount of acetonitrile to a 1,2-dichloroethane solution (acetonitrile/1,2-dichloroethane 1/9, v/v) the equilibrium (9) is established.



(9)

IIa : $\nu(CO)$ = 2093, 2035 cm^{-1} — 2005 cm^{-1}

IVa : $\nu(CO)$ = 2095, 2038 cm^{-1} — 2010 cm^{-1}

IVb : $\nu(CO)$ = 2098, 2043 cm^{-1} — 2020 cm^{-1}

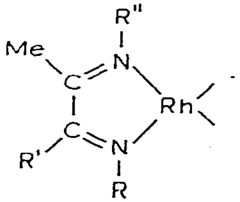
N-N = chelating diazabutadiene ligand; S = acetonitrile

The position of the equilibrium shifts to the right or to the left when N_2 or CO, respectively, is bubbled through the solution. The dicarbonyl species predominates in the solution of IIa and IVa, whereas the monocarbonyl species predominates in the solution of IVb, owing probably to a better shielding of the rhodium(I) center by the bulky diazabutadiene ligands in IIa and IVa. Electronic effects seem to play a minor role, as can be inferred from the similarity of the CO stretching frequencies.

The coordination of the 1,4-diaza-3-methylbutadien-2-yl moiety to rhodium(I) affects the typical IR and ^{1}H NMR bands of this group in the same way as the coordination of the transition metal ions in so far as these have been investigated [3—5]. The IR spectra of the free organometallic ligands DAB—DAB^{III} are characterized by two ν(C=N) bands in the range 1640—1550 cm^{-1}. Upon coordination these bands are shifted to lower frequency and markedly reduced in intensity, so that when the *N*-substituents are the p-C_6H_4OMe groups they can hardly be observed and/or assigned because of the strong absorptions of the *para*-substituted phenyl ring around 1600 and 1500 cm^{-1}. This is the case for all the rhodium(I) derivatives reported in Table 2, either containing a chelating or a bridging diazabutadiene ligand.

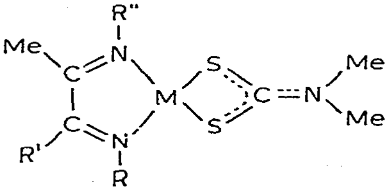
The ^{1}H NMR signals which are most influenced by coordination are those of the methyl group at position 3 on the diazabutadiene ligand and of the phenyl protons of p-C_6H_4OMe *N*-substituents. The latter usually appear as A_2B_2 (or $AA'BB'$) symmetrical multiplets having different patterns and chemical shifts according to the position of the p-C_6H_4OMe groups [4]. In many binuclear rhodium(I) compounds these signals partially overlap with the intense PPh_3 resonances as to prevent any detailed assignment. The A_2B_2 (or $AA'BB'$) multiplets are more easily observed for the trinuclear complexes V and the mononuclear derivatives IIIb and IVb (see Table 3).

In general, the signal of the methyl group at position 3 undergoes a marked down-field shift upon coordination as the result of various factors, such as inductive effects, the formation of a delocalised π electron system on the 5-membered ring and changes in the ligand configuration [3—5]. In complexes of the type:



the chemical shift of the methyl group, δ(C—Me), depends on the ancillary ligands at the rhodium(I) center and on the nature of substituent R′. For the dicarbonyl derivatives IIa, IVa and IVb the signal δ(C—Me) occurs at lower field (~0.2 ppm) relative to that of the corresponding COD analogues Ia, IIIa and IIIb.

The influence of the R′ group can be seen in the series of COD complexes IIIa, IIIb and Ia, all having R = R″ = p-C_6H_4OMe. The δ(C—Me) signal falls at 2.13 ppm for IIIa [R′ = PdCl(diphos)], at 2.12 ppm for IIIb (R′ = Me), but at considerably lower field, 2.77 ppm, for Ia [R′ = *cis*-$PdCl_2(PPh_3)$]. A similar trend is observed for the corresponding series of dicarbonyl derivatives IVa, IVb and IIa. A marked deshielding effect of the group R′ = *cis*-$PdCl_2(PPh_3)$ was also observed for the binuclear complexes [5].



R = R″ = p-C_6H_4OMe

M = Pd; δ(C—Me) = 2.88 ppm

M = Pt; δ(C—Me) = 2.60 ppm

In the 1,5-cyclooctadiene compounds I and III, the signals of the olefinic protons appear as an unresolved multiplet in the range 3.9—3.3 ppm, at significantly higher field than the corresponding signals (ca. 4.5 ppm) of the cationic complexes $[Rh(COD)(L—L)]^+$ (L—L = 2-aminomethylpyridine; 2,2′-bipyridine; 1,10-phenanthroline) [16].

TABLE 4

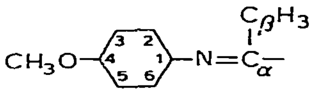
^{13}C NMR SPECTRA

In CD_2Cl_2; δ (ppm) from TMS.

DAB^{IV}	IIIb	Diazabutadiene carbons
169.0	181.0	C_α
15.58	20.28	C_β
144.9	138.18	C(1)
121.11	122.51	C(2,6)
114.86	114.74	C(3,5)
157.16	158.94	C(4)
56.01	55.73	OCH_3
		1,5-Cyclooctadiene carbons
	88.79 (^1J(RhC) 11.9 Hz)	=CH
	30.42	CH_2

The ^1H NMR spectra of the mononuclear complexes IIIb and IVb and the ^{13}C NMR spectra of IIIb and DAB^{IV} indicate that this ligand is symmetrically coordinated to rhodium(I) with two σ bonds through the imino nitrogen atoms.

The ^{13}C NMR spectra in CD_2Cl_2 are listed in Table 4.



The marked deshielding of C_α and C_β carbons upon coordination indicates that σ-donation is predominant in the rhodium(I)—DAB^{IV} bond [17]. In particular, the down-field shift (12 ppm) of the C_α signal is also indicative of σ *N*-bonded diazabutadiene ligands [11,17,18].

The electronic spectra in CH_2Cl_2 solution (700—250 mm) are shown in Fig. 2 for 1,5-cyclooctadiene derivatives Ia, Ib, IIIb, and in Fig. 3 for the dicarbonyl compounds IIa, IVb. For the mononuclear complexes IIIb and IVb the bands at wavelengths >300 nm are essentially due to electronic transition between the rhodium(I) *d* levels and the antibonding orbitals of the conjugated double bond system of the chelating diazabutadiene DAB^{IV} (CT bands), as suggested by the marked dependence on the ancillary ligands (COD or CO) at the rhodium(I) center and by solvatochromic effects. (The band maxima shift to higher frequency in more polar solvents, such as methanol and/or acetonitrile [17,19]). In the case of the dicarbonyl complex IVb, charge-transfer bands $d \rightarrow \pi^*$(CO) may also be present in the spectral range investigated [20].

Except for some variations in the band maxima, mainly due to the different *N*- and *C*-substituents in the N=CC=N group, the spectra of the 1,5-cyclooctadiene (Ia, Ib) and dicarbonyl (IIa) binuclear complexes are similar to those of

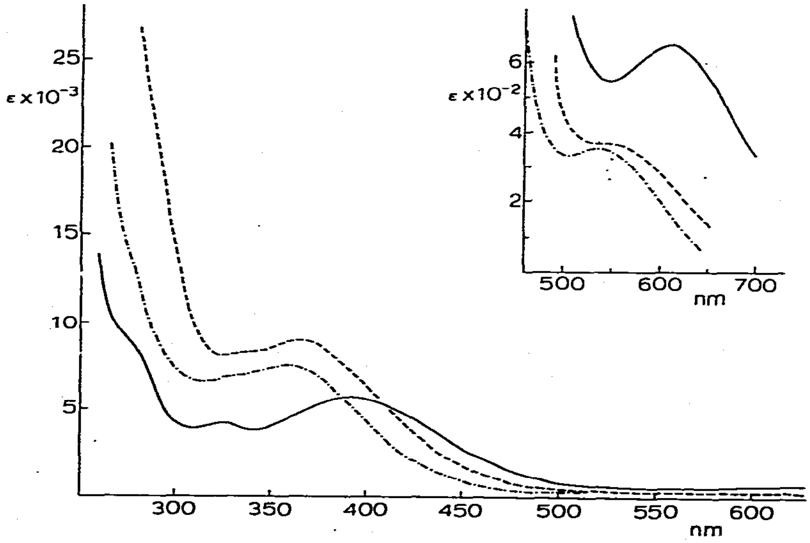


Fig. 2. Electronic spectra in CH_2Cl_2 of the 1,5-cyclooctadiene complexes Ia (— — — —), Ib (— · — · —) and IIIb (————).

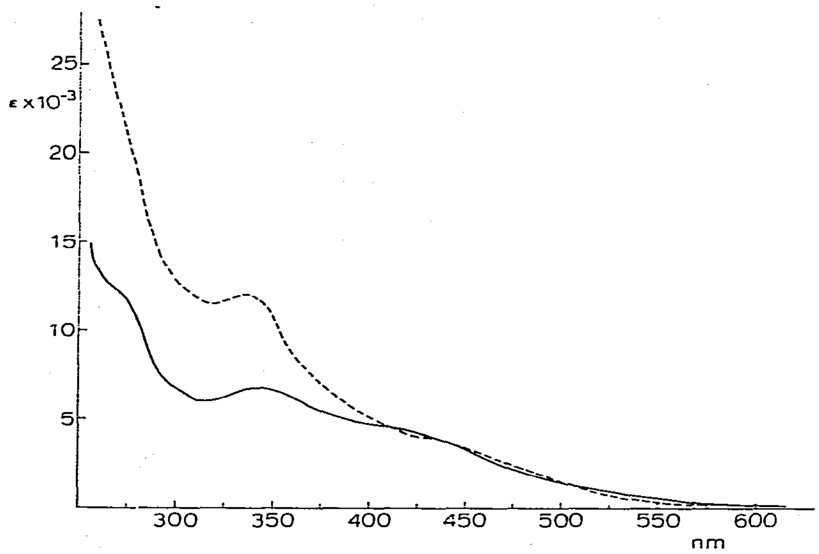


Fig. 3. Electronic spectra in CH_2Cl_2 of the dicarbonyl complexes IIa (— — — —) and IVb (————).

the corresponding mononuclear analogues IIIb and IVb, respectively, which unambiguously contain a *N*-chelating diazabutadiene ligand. This indicates that the same 5-membered metallocycle chromophore is present in both series of compounds and lends further support to the proposed structure for the zwitterionic complexes I and II.

Experimental

The complexes $[RhCl(COD)]_2$ and $[RhCl(CO)_2]_2$ were prepared by standard methods [8,21]. The 1,4-diazabutadiene ligands DAB—DAB^{IV} were prepared and purified by published methods [1—5,22]. All other chemicals were reagent grade, and used without further purification. Infrared spectra were recorded with Perkin—Elmer 457 (4000—250 cm^{-1}) and Beckman IR 11 (400—120 cm^{-1}) instruments. Hexachlorobutadiene mulls and NaCl plates were used in the range 4000—1300 cm^{-1} and Nujol mulls and CsI or thin polythene discs in the range 1700—120 cm^{-1}.

Electronic spectra in solution were recorded with a Bausch & Lomb Spectronic 210 UV spectrophotometer in the range 700—250 nm at 25°C, using quartz cells of 1 cm path length. ^1H NMR spectra were recorded with a Varian EM-390 90 MHz instrument and ^{13}C NMR spectra with a Bruker WP 60 FT.

Molecular weights were measured with a Mechrolab osmometer at 37°C in 1,2-dichloroethane. Elemental analyses were carried out by A. Berton and G. Biasoli at the Microanalytical Laboratory, Laboratorio Radioelementi C.N.R., Padova. All reactions and physical measurements in solution were carried out in deaerated solvents under N_2. Owing to the moderate stability of the new rhodium(I) complexes prepared in this work, fresh solutions of recently prepared samples were always used.

Reactions of $[RhCl(COD)]_2$ with $RN{=}C(R')C(Me){=}NR''$ (R' = trans-$PdCl(PPh_3)_2$; $R = R'' = p\text{-}C_6H_4OMe$ (DAB); $R = p\text{-}C_6H_4OMe$, R'' = Me (DAB^I))

(a) Pd/Rh ratio 1/2. A solution of the ligand DAB (0.474 g, 0.5 mmol) in ca. 50 ml of $CHCl_3$ was treated with $[RhCl(COD)]_2$ (0.247 g, 0.5 mmol). The colour immediately changed from golden-yellow to dark-green. After stirring for 1 h, the mixture was treated with charcoal, the filtrate was concentrated to small volume at reduced pressure and the product, Ia, was precipitated with diethyl ether. The compound was purified by reprecipitation from the same solvents (yield 0.400 g, 86% based on the theoretical amount). The mother liquor from the first precipitation was concentrated to small volume. Addition of n-hexane gave a yellow precipitate (0.17 g), identified as $[RhCl(COD)(PPh_3)]$ on the basis of its IR spectrum (ν(Rh—Cl) 285 cm^{-1}), ^1H NMR specrrum (olefinic protons resonances δ(—CH=) 6.1 and 3.2 ppm [6]) and elemental analysis (Found: C, 61.3; H, 5.5; Cl, 7.1. Calcd. for $C_{26}H_{27}ClPRh$: C, 61.37; H, 5.35; Cl, 6.97%.)

The reaction of DAB^I (0.428 g, 0.5 mmol) with $[RhCl(COD)]_2$ (0.247 g, 0.5 mmol) was carried out as described above for DAB to give the green product Ib (0.36 g, 86%) and $[RhCl(COD)(PPh_3)]$ (0.16 g).

(b) Pd/Rh ratio 1/1. When the reaction of DAB with $[RhCl(COD)]_2$ was carried out with a Pd/Rh ratio of 1/1, the IR spectrum of the reaction mixture in $CHCl_3$ showed the presence of unreacted DAB, characterised by two ν(C=N) bands at 1620 and 1560 cm^{-1}. The ^1H NMR spectrum of the same reaction mixture in $CDCl_3$ indicated the presence of three compounds, $[RhCl(COD)(PPh_3)]$, Ia and DAB in a molar ratio of ca. 1/1/1, the latter two complexes being easily identified by their characteristic δ(C—Me) signals at 1.29 and 2.77 ppm, respectively [1].

Reactions of the complexes I with PPh_3

The binuclear complexes I (0.1 mmol) were treated with PPh_3 (0.053 g, 0.2 mmol) in 1 ml of $CDCl_3$. The colour changed from dark-green to yellow and the ^1H NMR spectra of the reaction mixtures indicated a nearly quantitative formation of DAB (or DAB^I) and $[RhCl(COD)(PPh_3)]$.

Reactions of the complexes I with CO

The binuclear complex Ia (0.466 g, 0.5 mmol) was suspended in 10 ml of a toluene/n-hexane (4/1, v/v) mixture. Carbon monoxide was bubbled through the stirred suspension for 15 min, then the mixture was kept under CO atmosphere for 1 h. The red product IIa, was filtered off and washed with the same mixture of solvents (yield: 0.414 g, 94%). The reaction of Ib (0.420 g, 0.5 mmol) was carried out in the same way to give the yellow-orange product IIb (yield: 0.37 g, 94%).

Reaction of $[RhCl(COD)]_2$ with $RN{=}C(R')C(Me){=}NR''$ ($R = R'' = p\text{-}C_6H_4OMe$; $R' = Pd(dmtc)(PPh_3)$ (DAB^{II}))

The ligand DAB^{II} (0.385 g, 0.5 mmol) dissolved in ca. 50 ml of CH_2Cl_2 was treated with $[RhCl(COD)]_2$ (0.247 g, 0.5 mmol; ratio Pd/Rh 1/2). There was an immediate change of colour from yellow to dark-green. The mixture was worked up as in the case of the reaction with DAB to give a dark-green product (0.370 g), characterized as the binuclear complex Ia, and a brown solid (0.120 g) identified as an impure sample of [Rh(COD)(dmtc)] (ν(C=N) 1545 cm^{-1}). The ^{1}H NMR spectrum of the reaction mixture in CDCl$_3$ indicated a fast and quantitative formation of the products Ia and [Rh(COD)(dmtc)] in a molar ratio 1/1. An authentic sample of the latter compound was prepared from the reaction of [RhCl(COD)]$_2$ (0.247 g, 0.5 mmol) with Na[dmtc] · 2 H$_2$O (0.197 g, 1 mmol) in CH$_2$Cl$_2$/MeOH (3/1, v/v). After stirring for 1 h the solvents were evaporated to dryness and the solid residue was treated with benzene and charcoal. After filtration, the clear yellow solution was concentrated to small volume and the yellow-brownish product was precipitated by addition of diethyl ether/n-hexane (1/1, v/v). The compound was purified by reprecipitation from the same solvents (yield 0.20 g, 60%). Elemental analysis: Found: C, 39.5; H, 5.4; N, 4.3. Calcd. for C$_{11}$H$_{18}$NS$_2$Rh: C, 39.88; H, 5.47; N, 4.23%. Characteristic IR bands: ν(C=N) 1543s(br); ν(Rh—S) 369m, 360m. The ^{1}H NMR spectrum is reported in Table 3.

Reaction of [RhCl(COD)]$_2$ with RN=C(R')C(Me)=NR" (R = R" = p-C$_6$H$_4$OMe; R' = PdCl(diphos) (DAB^{III}))

The reaction of [RhCl(COD)]$_2$ with DAB^{III} (Pd/Rh ratio 1/2) was carried out as described for the reaction with DAB. A dark-green product was obtained, the elemental analysis of which approximately corresponded to that of the ionic compound [Rh(COD)(DAB^{III})][RhCl$_2$(COD)]. Anal.: (Found): C, 52.5; (53.5); H, 4.2, (4.7); N, 2.1, (2.4); Cl, 7.8, (7.7). Calcd. for C$_{59}$H$_{65}$Cl$_3$N$_2$O$_2$P$_2$PdRh$_2$: C, 53.9; H, 4.98; N, 2.13, Cl, 8.09%. No better analytical data were obtained even after several reprecipitations from CHCl$_3$ (or CHCl$_3$/MeOH mixtures) and diethyl ether.

The ^{1}H NMR spectrum of the reaction in CDCl$_3$ indicated a fast and quantitative formation of an equimolar mixture of the cation [Rh(COD)(DAB^{III})]$^+$ and the anion [RhCl$_2$(COD)]$^-$. Conductivity measurements at 20°C on the reaction mixture in methanol [obtained by mixing DAB^{III} (0.041 g, 0.05 mmol) and [RhCl(COD)]$_2$ (0.024 g, 0.05 mmol) in 50 ml of MeCH] showed a conductivity of 8.85×10^{-5} ohm^{-1} with a cell constant K 0.813 cm^{-1}. This corresponds to a molar conductivity Λ_M 72 ohm^{-1} cm^2 mol^{-1} if the reaction quantitatively yields a 10^{-3} M solution of the ionic compound [Rh(COD)(DAB^{III})][RhCl$_2$(COD)]. An authentic sample of the anionic complex [RhCl$_2$(COD)]$^-$ as tetraphenylarsonium salt was prepared from the reaction of [RhCl(COD)]$_2$ (0.161 g, 0.33 mmol) with AsPh$_4$Cl (0.280 g, 0.66 mmol) in CH$_2$Cl$_2$. After stirring for 30 min the mixture was treated with charcoal and filtered. The clear filtrate was concentrated to small volume and the pale-yellow product was precipitated by addition of diethyl ether/n-hexane (1/1, v/v) (yield 0.30 g, 68%). Elemental analysis: Found: C, 57.0; H, 4.8; Cl, 10.7. Calcd. for C$_{32}$H$_{32}$AsCl$_2$Rh: C, 57.76; H, 4.85; Cl, 10.66%.Molar conductivity Λ_M 73.2 ohm^{-1} cm^2 mol^{-1} for a 10^{-3} M solution in MeOH at 20°C. The ^{1}H NMR spectral data are shown in Table 3.

Reactions of [Rh(Cl(COD)]$_2$ with RN=C(R')C(Me)=NR" (R = R" = p-C$_6$H$_4$OMe; R' = PdCl(diphos) (DAB^{III}); R' = Me (DAB^{IV})) and NaClO$_4$

The ligand DAB^{III} (0.411 g, 0.5 mmol) suspended in MeOH (20 ml) was treated with [RhCl(COD)]$_2$ (0.123 g, 0.25 mmol; Pd/Rh ratio 1/1). The mixture was stirred for 30 min until complete dissolution of the yellow compound

DAB^{III}, then a solution of $NaClO_4 \cdot H_2O$ in ca. 5 ml of distilled water was added dropwise. Within 10 min the dark-green product IIIa began to precipitate. When the precipitation was completed (30—60 min), the microcrystalline solid was filtered off and washed with distilled H_2O, then with a mixture H_2O/MeOH (1/1, v/v), and finally with cold MeOH (yield 0.425 g, 75%).

The same procedure was followed for the reaction with DAB^{IV}. In this case a longer time was required for the complete dissolution of the ligand (yield of product IIIb 89%).

Reactions of the complexes III with CO

The complex IIIa (0.566 g, 0.5 mmol) was suspended in MeOH (10 ml) and carbon monoxide was bubbled through the stirred mixture for 15 min. During this time the dark-green solid dissolved completely to give a dark-red solution from which the product IVa separated as a dark-blue microcrystalline solid. This was filtered off and washed with cold MeOH (yield 0.416 g, 77%).

The reaction of IIIb (0.303 g, 0.5 mmol) was carried out in the same way to yield the dark-brown product IVb (0.216 g, 78%). The carbon monoxide content in complexes IV was determined by the method described by Schrock and Osborn [9], using 1,2-dichloroethane as solvent, instead of 2-butanone. The volume of evolved CO was the 95% of theory for IVa, and the 104% of theory for IVb.

Reactions of $[RhCl(CO)_2]_2$ *with* $RN{=}C(R')C(Me){=}NR''$ (R' = *trans*-$PdCl(PPh_3)_2$; $R = R''$ = p-C_6H_4OMe *(DAB)*; R = p-C_6H_4OMe, R'' = Me *(DAB*^{I}*))*

(a) Pd/Rh ratio 1/2. The ligand DAB (0.474 g, 0.5 mmol) suspended in toluene (25 ml) was treated with $[RhCl(CO)_2]_2$ (0.195 g, 0.5 mmol). A clear dark-red solution was obtained, from which a red compound began to precipitate after stirring for ca. 30 min. The mixture was left aside for 2 h, then the product Va was filtered off and washed with cold toluene (yield 0.535 g, 80%).

The reaction of DAB^I (0.443, 0.5 mmol) with $[RhCl(CO)_2]_2$ (0.195 g; 0.5 mmol) was carried out similarly to give the red-orange product Vb (0.53 g, 85%). In this case a toluene/n-hexane (4/1, v/v) mixture was used as solvent.

(b) Pd/Rh ratio 1/1. When the reaction of DAB with $[RhCl(CO)_2]_2$ was carried out with a ratio Pd/Rh of 1/1, the IR spectrum of the reaction mixture in $CHCl_3$ (2 min after mixing of the reactants) showed the immediate formation of Va [ν(CO) 2100, 2074, 2044, 1933 cm^{-1}] and the presence of unreacted DAB [ν(C=N) 1620, 1560 cm^{-1}]. On standing, a subsequent slower reaction took place, which in ca. 1 h led to the formation of the complex IIa [ν(CO) 2093, 2036 cm^{-1}] and of a small amount of *trans*-$[RhCl(CO)(PPh_3)_2]$ [ν(CO) 1978 cm^{-1}].

The same reaction in $CDCl_3$ was followed by ^1H NMR spectroscopy. The initial spectrum (4 min after mixing of DAB and $[RhCl(CO)_2]_2$) indicated the presence of the compounds Va and DAB in a molar ratio ~1/1 [δ(C—Me) 2.42 and 1.29 ppm, respectively]. On standing, the complex Va disappeared slowly with the concomitant formation of IIa [δ(C—Me) 2.96 ppm]. At the same time a decrease of DAB concentration was observed. When the reaction was completed (ca. 1 h), the mixture contained the complex IIa as major product, a smaller amount of unreacted DAB and some unidentified minor products, characterized by weak δ(C—Me) and δ(O—Me) signals in the ranges 2.7—2.1 and 3.9—3.5 ppm respectively.

Reaction of Va with PPh_3

The complex Va (0.334 g, 0.25 mmol) dissolved in 1,2-dichloroethane (10 ml) was treated with PPh_3 (0.064 g, 0.25 mmol). As indicated by IR spectra at various times, a slow reaction occurred yielding the products IIa and *trans*-$[RhCl(CO)(PPh_3)_2]$ in ca. 90 min. The mixture was concentrated to small volume (ca. 3 ml) and set aside overnight. Yellow crystals of *trans*-$[RhCl(CO)(PPh_3)_2]$ formed, and were filtered off and identified by elemental analysis and IR spectra [ν(CO) 1965 cm^{-1} and ν(Rh—Cl) 311 cm^{-1}].

The ^1H NMR spectra of the reaction mixture in $CDCl_3$ (molar ratio Va/PPh_3 1/1) showed almost quantitative formation of complex IIa when the reaction was complete.

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