(2,5-Norbornadiene)rhodium(I) Complexes with Bis- and Tris(azol-1-yl)methanes

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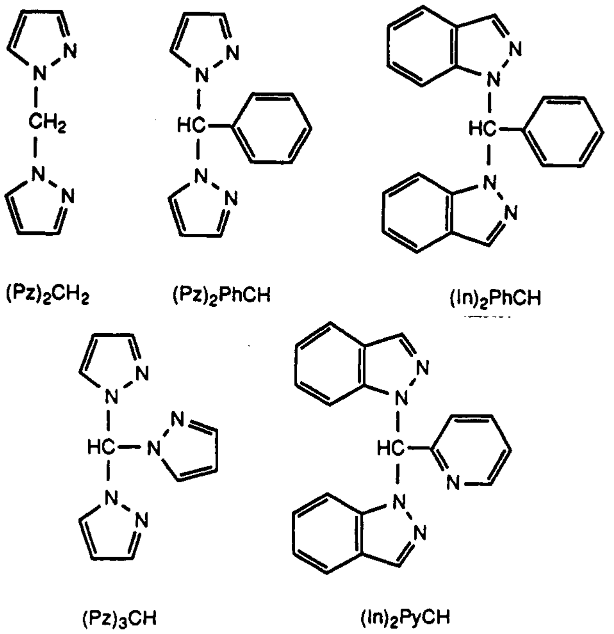
Reactions of bis[(2,3,5,6-η)-bicyclo[2.2.1]hepta-2,5-diene]bis(μ-chloro)dirhodium, [RhCl(NBD)]$_2$, with bis- and tris(azolyl)methanes have been performed in methanol and acetone with 1:1 and 1:2 [RhCl(NBD)]$_2$/ligand molar ratios. The structures of the complexes have been characterized by infrared and ^{1}H and ^{13}C NMR spectroscopy as well as X-ray diffraction analysis. Cationic species have been evidenced in the solid state while equilibria between cationic and neutral species have been established in solution.

Introduction

Polyazolylmethanes are excellent ligands of rhodium(I). In particular, pyrazole and indazole derivatives such as $(Pz)_2CH_2$, $(Pz)_2PhCH$, $(Pz)_3CH$, and $(In)_2PyCH$ (Pz = pyrazole, 3,5-dimethylpyrazole, and 4-bromopyrazole; In = indazole; Py = pyridin-2-yl) form stable rhodium(I) complexes.[2–5] The coordination behavior of the azole ring in the ligands is different, and a variety of species have been obtained. Depending on the reaction conditions, ligands behave either as bidentate bridged chelates or tridentates to yield structures with square-planar or trigonal-bipyramidal coordination. In these previous studies a large number of rhodium(I) complexes with 1,5-cyclooctadiene (COD) as diolefinic ligand were described, but very little information exists concerning complexes which contain the higher π-acceptor 2,5-norbornadiene (NBD) as diolefinic ligand.

In this work we perform a systematic study of the reaction of bis[(2,3,5,6-η)-bicyclo[2.2.1]hepta-2,5-diene]bis(μ-chloro)dirhodium [RhCl(NBD)]$_2$[6] with bi- or tridentate polyazolylmethanes shown in Chart 1 as ligands (L). The aim is to analyze which type of complex is obtained depending on the nature of the ligand and on the reaction conditions.

Chart 1



Furthermore, taking into account that ligands such as bis(pyrazol-1-yl)phenylphosphine and the structurally related $(Pz)_2PhCH$ gave unsaturated carbonyl complexes in which a coordination position was blocked by the phenyl group,[7,8] $(Pz)_2PhCH$ and $(In)_2PhCH$ ligands have been selected with the purpose of obtaining rhodium–phenyl interactions similar to those described in the active species of Wilkinson's catalyst.[9]

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Table 1. IR Data, Molar Conductivity, Isolated Yield, Color, and Elemental Analyses of [Rh(NBD)(L)]PF_6

						calcd			found		
L	IR (cm^{-1})[a]	Λ_M ($\times 10^{-4}$ S m^2 mol^{-1})	yield (%)	color	molecular formula	C	H	N	C	H	N
$(Pz)_2CH_2$	840 (νPF) 555 (δ FPF)	88[b]	83	yellow	$C_{14}H_{16}F_6N_4PRh$	34.43	3.28	11.48	34.56	3.18	11.40
$(Pz)_2PhCH$	850–830 (ν PF) 560 (δ FPF)	110[b]	70	yellow	$C_{20}H_{20}F_6N_4PRh$	42.56	3.55	9.93	42.68	3.55	9.75
$(In)_2PhCH$	850–830 (ν PF) 560 (δ FPF)	130[b]	83	yellow	$C_{28}H_{24}F_6N_4PRh$	50.61	3.61	8.43	49.65	3.60	8.01
$(Pz)_3CH$	830 (ν PF) 560 (δ FPF)	146[b]	80	yellow	$C_{17}H_{17}F_6N_6PRh$	36.86	3.25	15.17	36.70	3.20	14.95
$(In)_2PyCH$[c]	840, 760 (ν PF)	65[d]	47	yellow							

[a] In KBr. [b] In acetone solution. [c] From ref 5. [d] In nitromethane solution.

Table 2. ^1H NMR Chemical Shifts of Ligands (L) and Their [Rh(NBD)(L)]PF_6 complexes in DMSO-d_6 (Coordination-Induced Shifts (CIS) in Parentheses)[a]

compd	H_3	H_4	H_5	H_6	H_7	C(sp^3)H	H_{ortho}	H_{meta}	H_{para}	NBD protons
$(Pz)_2CH_2$	7.49	6.28	7.93			6.50				
[Rh(NBD){$(Pz)_2CH_2$}]PF_6	7.66	6.55	8.13			6.64				CH_2-7: 1.34 CH-2,3,5,6: 4.48 CH-1,4: 3.99
	(+0.17)	(+0.27)	(+0.20)			(+0.26)				
$(Pz)_2PhCH$	7.60	6.36	7.86			8.07	7.38	7.03	7.37	
[Rh(NBD){$(Pz)_2PhCH$}]PF_6	7.79	6.69	8.49			8.54	6.42	7.59[d]		CH_2-7: 1.13 CH-2,3,5,6: 4.04 CH-1,4: 3.60
	(+0.19)	(+0.33)	(+0.63)			(+0.47)	(–0.96)	(+0.56)	(+0.22)	
$(In)_2PhCH$	8.18	7.77	*b*	*c*	7.66	8.92	7.34	7.14	7.34	
[Rh(NBD){$(In)_2PhCH$}]PF_6	8.47	7.92	7.40	7.76	8.43	9.44	6.45	7.59[d]		CH_2-7: 1.15 CH-2,3,5,6: 4.14 CH-1,4: 3.60
	(+0.29)	(+0.15)			(+0.77)	(+0.52)	(–0.89)	(+0.45)	(+0.25)	
$(Pz)_3CH$	7.68	6.42	7.90			8.99				
[Rh(NBD){$(Pz)_3CH$}]PF_6	8.16	6.53	8.28			9.50				CH_2-7: 1.18 CH-2,3,5,6: 3.58 CH-1,4: 3.78
	(+0.48)	(+0.11)	(+0.38)			(+0.51)				

[a] Coupling constant values are in the normal range and are omitted. [b] Masked by *meta* protons. [c] Masked by *ortho* protons. [d] H_{meta}, H_{para}.

Results and Discussion

Reactions of dimer [RhCl(NBD)]$_2$ with the ligands depicted in Chart 1 were performed in two different polarity solvents (methanol and acetone) and two different dimer:ligand molar ratios (1:2 and 1:1). In spite of the use of the Schlenk technique in previous work, we have found that it is not necessary to carry out the reactions in an inert atmosphere.

Reaction in Methanol. All ligands reacted with [RhCl(NBD)]$_2$ in a dimer:ligand molar ratio of 1:2 in methanol to give the corresponding ionic species [Rh(NBD)(L)]$^+$, which were isolated in high yield as stable salts [Rh(NBD)(L)]$^+$$PF_6^-$. These results are in agreement with those obtained in the reaction of [RhCl(diolefin)]$_2$ with monodentate ligands in a high-polarity solvent in which ionic complexes are obtained through an ion chloride displacement.[10] The low nucleophilicity of the PF_6 counterion produces a stabilization of the cationic structure. Such extrastabilization is not observed in the neutral polypyrazolylborate complex analogues in which fluxional phenomena are observed.[11]

The ionic structure and the rhodium(I) coordination are well characterized by conductivity measurements and infrared (Table 1) and ^1H and ^{13}C NMR spectroscopy (Tables 2 and 3). In addition, the crystalline structure of [Rh(NBD){$(Pz)_2PhCH$}]PF_6 has been determined by X-ray diffraction analysis.

Tetracoordination of the type (NN)Rh(NBD) in complexes [Rh(NBD){$(Pz)_2CH_2$}]PF_6, [Rh(NBD){$(Pz)_2PhCH$}]PF_6, and [Rh(NBD){$(In)_2PhCH$}]PF_6 and pentacoordination of the type (NNN)Rh(NBD) in [Rh(NBD){$(Pz)_3CH$}]PF_6 were easily identified in the ^1H NMR spectra considering the NBD proton resonances. In those complexes in which tetracoordination was implied, H_1 and H_4 resonated at higher frequency than the olefinic H_2, H_3, H_5, and H_6 protons. The same feature was observed in [RhCl(NBD)]$_2$.[12] In contrast, the tridentate ligand $(Pz)_3CH$ gave a pentacoordinate complex in which H_1 and H_4 protons resonated at lower frequency than the olefinic protons. This feature was also found in [Rh(NBD){$(In)_2PyCH$}], a complex previously described by us,[5] and can be used to assign unambiguously the (NNN)Rh(NBD) pentacoordination. This intrinsic property of NBD represents a substantial advantage with respect to the COD used in previous complexes as ancillary ligand.[4a]

Tetra- and pentacoordinate complexes also presented significant differences in the ^{13}C NMR of NBD carbons (Table 3). Assignments of these carbons were obtained with the help of DEPT sequences. Carbon–Rhodium coupling constant values followed the sequence $^1J(C_{2,3,5,6}\text{-}Rh) > {}^3J(C_7Rh) > {}^2J(C_{1,4}Rh)$ for all complexes including

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(12) Only ^1H NMR data in $CDCl_3$ at 60 MHz are reported: δ(CH-1,4) and δ(CH-2,3,5,6), 3.96 ppm; δ(CH_2-7), 1.21 ppm.[13] We have repeated ^1H NMR (200.13 MHz, $CDCl_3$): δ(CH-2,3,5,6), 3.91 ppm; δ(CH-1,4), 3.81 ppm; δ(CH_2-7), 1.18 ppm. ^{13}C NMR (50.33, $CDCl_3$): $\delta(C_{1,4})$, 49.92; $J_{(CRh)}$, 3.0 Hz; $\delta(C_{2,3,4,6})$, 51.49 ppm; $J_{(CRh)}$, 11.0; $\delta(C_7)$, 60.53; $J_{(CRh)}$, 7.1 Hz.

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Table 3. ^{13}C NMR Data of Ligands (L) and Their $[Rh(NBD)(L)]PF_6$ Complexes (Coordination-Induced Shifts (CIS) in Parentheses)

compd	C_3	C_{3a}	C_4	C_5	C_6	C_7	C_{7a}	C(sp^3)	C_{ipso}	C_{ortho}	C_{meta}	C_{para}	NBD carbons
$(Pz)_2CH_2$[a]	140.1		106.3	130.5				64.4					
$[Rh(NBD)\{(Pz)_2CH_2\}]PF_6$[a]	142.8		107.2	134.5				62.5					C_7: 62.3 $C_{2,3,5,6}$: 59.5; J_{Rh} = 10.1 $C_{1,4}$: 50.6; J_{Rh} = 1.5
	(+2.7)		(+0.9)	(+4.0)				(−1.9)					
$(Pz)_2PhCH$[a]	140.1		106.2	130.3				76.2	137.0	128.5	126.8	128.8	
$[Rh(NBD)\{(Pz)_2PhCH\}]PF_6$[a]	143.3		107.4	135.3				74.3	136.6	125.3	129.0	129.6	C_7: 62.0; J_{Rh} = 6.2 $C_{2,3,5,6}$: 59.8 (bs) $C_{1,4}$: 50.2; J_{Rh} = 1.9
	(+3.2)		(+1.2)	(+5)				(−1.9)	(−0.4)	(−3.2)	(+2.2)	(+0.8)	
$(In)_2PhCH$[a]	134.6	124.2	121.3	121.0	126.6	110.7	139.6	72.8	135.9	128.4	127.5	128.5	
$[Rh(NBD)\{(In)_2PhCH\}]PF_6$[a]	139.0	123.6	122.1	122.0	130.7	109.7	140.4	69.2	136.6	126.0	129.3	129.6	C_7: 62.0; J_{Rh} = 5.6 $C_{2,3,5,6}$: 59.8; J_{Rh} = 9.8 $C_{1,4}$: 50.3
	(+4.4)	(−0.6)	(+0.8)	(+1.0)	(+4.1)	(−1.0)	(+0.8)	(−3.6)	(+0.7)	(−2.4)	(+1.8)	(+1.1)	
$(Pz)_3CH$[a]	140.9		106.9	130.2				81.6					
$[Rh(NBD)\{(Pz)_3CH\}]PF_6$[a]	143.5		107.4	133.3				75.2					C_7: 75.2[b] $C_{2,3,5,6}$: 58.2; J_{Rh} = 6.8 $C_{1,4}$: 47.3; J_{Rh} = 2.7
	(+2.6)		(+0.5)	(+3.1)				(−6.4)					
$(Pz)_3CH$[c]	141.7		107.2	129.4				83.2					
$[Rh(NBD)\{(Pz)_3CHM\}]PF_6$[c]	142.6		107.8	132.9				75.7					C_7: 58.5; J_{Rh} = 6.7 $C_{2,3,5,6}$: 38.9; J_{Rh} = 10.7 $C_{1,4}$: 47.9; J_{Rh} = 2.5
	(+0.9)		(+0.6)	(+3.5)				(−7.5)					

[a] In DMSO-d_6; bs, broad signal. [b] Overlapped by C(sp^3) signal. [c] In $CDCl_3$.

the dimer $[RhCl(NBD)]_2$.[12] In our previous publication on $[Rh(NBD)\{(In)_2PyCH\}]PF_6$,[5] the absence of previous data caused a misassignment in the C_7 and $C_{1,4}$ carbons. The fact that $J(C_7Rh) > J(C_{1,4}Rh)$ can be explained as a consequence of pseudo-*endo*-configuration of the Rh–NBD bond, as in the case of *endo*-norborn-2-yl trimethylstannanes in which $J(C_7Sn) > J(C_{1,4}Sn)$.[14] The chemical shifts depended on the solvent. While in DMSO-d_6 the chemical shift of all complexes followed the sequence $\delta(C_7) > \delta(C_{2,3,5,6}) > \delta(C_{1,4})$, in $CDCl_3$ the $C_{2,3,5,6}$ carbons of the pentacoordinate complexes resonated at the highest frequency: $\delta(C_7) > \delta(C_{1,4}) > \delta(C_{2,3,5,6})$.

The expected rhodium–phenyl interactions in complexes $[Rh(NBD)\{(Pz)_2PhCH\}]PF_6$ and $[Rh(NBD)\{(In)_2PhCH\}]PF_6$ would be inferred by the observed shielding effect of the rhodium atom on protons and carbons on the *ortho* position of the phenyl group.[15] In fact, in both complexes *ortho* protons and carbons resonate at higher field than the corresponding protons and carbons in the ligands ($\Delta\delta_H = -0.96$ ppm, $\Delta\delta_C = -3.2$ ppm, and $\Delta\delta_H = -0.89$ ppm, $\Delta\delta_C = -2.4$ ppm, respectively; $\Delta\delta = \delta_{complex} - \delta_{ligand}$).

This type of interactions has been observed also in the crystalline structures of a bis(pyrazolyl)phenylmethane molybdenum complex[8] and triphenylphosphine rhodium complexes.[9]

The X-ray crystalline structure of $[Rh(NBD)\{(Pz)_2PhCH\}]PF_6$ (Table 4) revealed a monomeric square-planar cationic species formed by the rhodium atom, the two nitrogen atoms of the pyrazole rings, and the centroids G1 and G2 of the double bonds of the NBD ligand. This tetracoordination gives a metallocycle $Rh(NN)_2C1$ with a boat conformation, in which the phenyl group attached to carbon atom C1 is located in an *endo*-position with respect to the rhodium atom (Figure 1). In this situation the phenyl group is closer to the rhodium atom than it would be if oriented in the *exo*-position. Consequently, the π-electrons of the aromatic ring would enter the coordination sphere of the metal. In this way the tetracoordinatively-unsaturated 16-electron complex would be stabilized as a pseudopentacoordinatively-saturated 18-electron complex.[16]

Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) of the Complex $[Rh(NBD)\{(Pz)_2PhCH\}]PF_6$ (with Esd's)

Bond Lengths			
Rh–N11	2.08(2)	C31–C32	1.57(5)
Rh–N21	2.10(2)	C31–C36	1.33(5)
Rh–C31	2.08(3)	C32–C33	1.42(5)
Rh–C33	2.09(3)	C32–C37	1.54(5)
Rh–C34	2.09(3)	C33–C34	1.36(5)
Rh–C36	2.07(3)	C34–C35	1.49(5)
N12–C1	1.47(3)	C35–C36	1.60(4)
N22–C1	1.53(3)	C35–C37	1.59(5)
C1–C2	1.50(3)		
Rh–C2	3.23(2)		
Rh–C7	3.65(4)		
Rh–H1	4.20		
Rh–G1[a]	1.97(3)		
Rh–G2[a]	1.97(3)		
Bond Angles			
C34–Rh–C36	68(1)	N11–Rh–C34	160(1)
C33–Rh–C36	80(1)	N11–Rh–C33	159(1)
C33–Rh–C34	38(1)	N11–Rh–C31	101(1)
C31–Rh–C36	37(1)	N11–Rh–N21	85(1)
C31–Rh–C34	79(1)	N12–C1–N22	110(2)
C31–Rh–C33	65(1)	H1–C1–N22	112(2)
N21–Rh–C36	161(1)	H1–C1–N12	107(2)
N21–Rh–C34	101(1)	N22–C1–C2	110(2)
N21–Rh–C33	103(1)	N12–C1–C2	114(2)
N21–Rh–C31	160(1)	H1–C1–C2	103(2)
N11–Rh–C36	99(1)		

[a] G1 = centroid (C31–C36), G2 = centroid (C33–C34).

In spite of the distances Rh–C2 (3.23(4) Å), Rh–C7 (3.65(4) Å), and Rh–C3 (3.75(3) Å) as well as the N12C1C2C7 and N12C1C2C3 torsion angles (26° and 155°) not allowing rhodium–phenyl interaction, it is possible to expect that this situation would change in solution. The phenyl group, due to free rotation in solution, would adopt an adequate orientation to allow the rhodium–phenyl interaction detected in the ^1H and ^{13}C NMR spectra.

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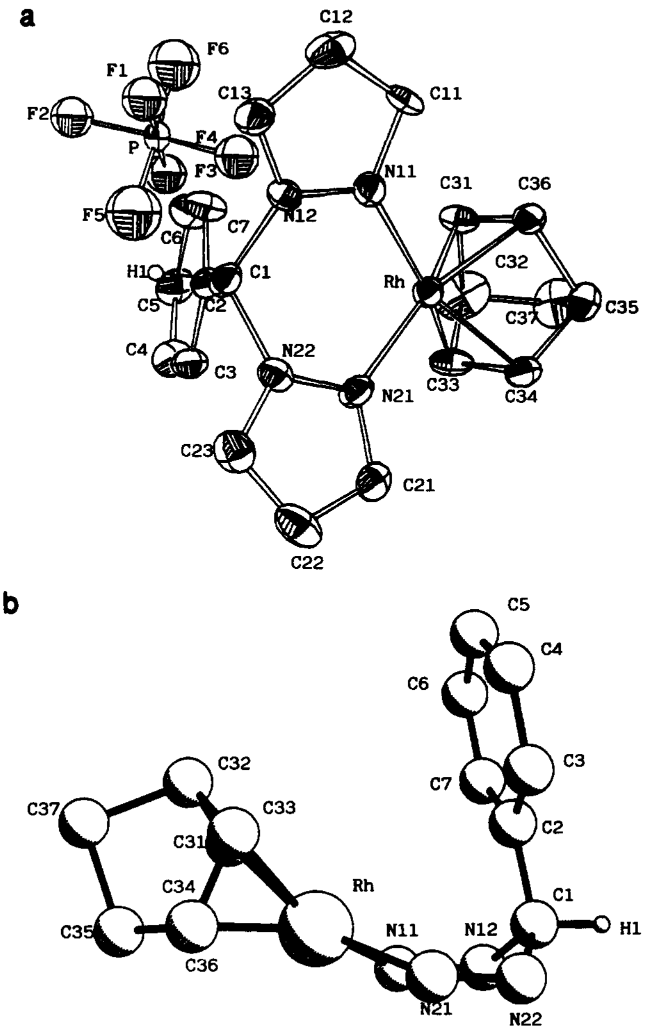

Figure 1. (a) Perspective ORTEP[18] view of $[Rh(NBD)\{(Pz)_2PhCH\}]PF_6$ with atomic numbering scheme. H atoms are omitted, and thermal ellipsoids are at the 70% probability level. (b) A PLUTO plot of the RhN11N12C1N21N22 metallocycle. Pyrazole carbons are omitted for clarity.

Table 5. IR data, Molar Conductivity, Isolated Yield, Color, and Elemental Analyses of Rhodium Complexes Obtained in Acetone

compd	IR (cm^{-1})^a	Λ_M (×10^{-4} S m^2 mol^{-1})	yield (%)	color	molecular formula	calcd C	calcd H	calcd N	found C	found H	found N	molar ratio $[RhCl(NBD)]_2$:ligand
$[\{RhCl(NBD)\}_2\{(Pz)_2CH_2\}]$	250 (ν RhCl)	55^b	72	yellow	$C_{21}H_{24}N_4Rh_2Cl_2$	41.40	3.94	9.20	41.15	3.90	9.07	1:1 and 1:2
$[\{RhCl(NBD)\}_2\{(Pz)_2PhCH\}]$	270–250 (ν RhCl)	33^c/94^d	71	orange	$C_{27}H_{28}N_4Rh_2Cl_2$	47.32	4.09	8.18	46.98	4.10	8.06	1:1
$[RhCl(NBD)\{(Pz)_2PhCH\}]$	260 (ν RhCl)	32–36^c	77	yellow	$C_{20}H_{20}N_4RhCl\cdot{}^1/_2H_2O$	51.80	4.53	12.08	51.49	4.54	11.90	1:2
$[Rh(NBD)\{(In)_2PhCH\}][RhCl_2(NBD)]$	250–240 (ν RhCl)	30–34^c	82	yellow	$C_{35}H_{32}N_4Rh_2Cl_2$	53.52	4.08	7.14	52.65	4.03	6.86	1:1 and 1:2
$[Rh(NBD)\{(In)_2PyCH\}][RhCl_2(NBD)]$	250 (ν RhCl)	32^c	75	yellow	$C_{34}H_{31}N_5Rh_2Cl_2$	51.93	3.94	8.91	51.30	3.80	8.37	1:1
$[Rh(NBD)\{(In)_2PyCH\}]Cl$	e	34^c	71	yellow	$C_{27}H_{23}N_5RhCl$	58.34	4.14	12.60	57.84	3.95	12.35	1:2
$[Rh(NBD)\{(Pz)_3CH\}][RhCl_2(NBD)]$	260 (ν RhCl)	20^b	64	orange	$C_{24}H_{26}N_6Rh_2Cl_2$	42.66	3.85	12.44	42.40	3.80	12.35	1:1
$[Rh(NBD)\{(Pz)_3CH\}]Cl$	e	6^b	76	pale yellow	$C_{17}H_{18}N_6RhCl$	45.89	4.04	18.89	45.70	3.98	18.72	1:2

[a] In KBr. [b] In acetone solution. [c] In ethanol solution. [d] In methanol solution. [e] ν RhCl was not observed.

Reactions in Acetone. All ligands reacted with the dimer $[RhCl(NBD)]_2$ in two dimer:ligand molar ratios: 1:1 and 1:2. Complexes crystallized from the reaction media to yield yellow or orange solids (Table 5). $(Pz)_2CH_2$ and $(In)_2PhCH$ gave the same species in both molar ratios, but the other ligands yielded different complexes depending on the molar ratio. Reaction of $(Pz)_2CH_2$ was previously carried out in a 1:1 molar ratio,[3] and the $[\{RhCl(NBD)\}_2\{(Pz)_2CH_2\}]$ complex was described. Although no spectroscopical data were given, a complex with a pyrazole bridge between two equivalent RhCl(NBD) species was suggested. We have repeated the reaction, and a complex with the same molecular formula as that reported was obtained in both molar ratios (Table 5). ^1H and ^{13}C NMR spectra (Tables 6 and 7) showed the equivalence of protons and carbons of both pyrazole rings as well as the presence of only three signals for NBD protons and carbons. This situation is also observed in the complex $[\{RhCl(NBD)\}_2\{(Pz)_2PhCH\}]$ obtained with $(Pz)_2PhCH$ in a 1:1 molar ratio.

An X-ray diffraction study of the latter compound indicated that the crystalline structure is an ion-pair species of the mononuclear cation $[Rh(NBD)\{(Pz)_2PhCH\}]^+$ and anion $[RhCl_2(NBD)]^-$ (Table 8). The monomeric square-planar cationic species is formed by

Table 6. ^{1}H NMR Chemical Shifts of Ligands (L) and Their Rhodium Complexes Obtained in Acetone (Coordination-Induced Shifts (CIS) in Parentheses)[a]

compd	H_3	H_4	H_5	H_6	H_7	C(sp^3)H	H_{ortho}	H_{meta}	H_{para}	NBD protons
$(Pz)_2CH_2$[b]	7.55	6.29	7.65			6.30				
$[\{RhCl(NBD)\}_2\{(Pz)_2CH_2\}]$[b]	7.09	6.30	8.71			7.12				CH_2-7: 1.30 CH-2,3,5,6: 4.04 CH-1,4: 3.87
	(−0.46)	(+0.01)	(+1.06)			(+0.82)				
$(Pz)_2PhCH$[c]	7.60	6.36	7.86			8.07	7.38	7.03	7.37	
$[Rh(NBD)\{(Pz)_2PhCH\}][RhCl_2(NBD)]$[c]	7.72	6.56	8.28			8.47	6.65	7.52[d]		CH_2-7: 1.24 CH-2,3,5,6: 4.19 CH-1,4: 3.75
	(+0.12)	(+0.2)	(+0.42)			(+0.40)	(−0.73)	(+0.49)	(+0.15)	
$[RhCl(NBD)\{(Pz)_2PhCH\}]$[c]	7.69	6.51	8.15			8.35	6.76	7.48[d]		CH_2-7: 1.22 CH-2,3,5,6: 4.16 CH-1,4: 3.72
	(+0.09)	(+0.15)	(+0.29)			(+0.28)	(−0.62)	(+0.45)	(+0.11)	
$(In)_2PhCH$[b]	8.07	7.69	7.12	7.31	7.50	8.50	7.31	7.12	7.31	
$[Rh(NBD)\{(In)_2PhCH\}][RhCl_2(NBD)]$[b]	8.08		7.35[e]		7.76	9.80	7.02	7.35[d]		CH_2-7: 1.24; 1.17 CH-2,3,5,6: 3.91; 3.60 CH-1,4: 3.82; 3.29
	(+0.01)	(−0.34)	(+0.23)	(+0.04)	(+0.26)	(+1.30)	(−0.29)	(+0.23)	(+0.04)	

							pyridine protons				
compd	H_3	H_4	H_5	H_6	H_7	C(sp^3)H	$H_{3'}$	$H_{4'}$	$H_{5'}$	$H_{6'}$	NBD protons
$(In)_2PyCH$[b]	8.10	7.71	7.14	7.31	7.50	8.46	7.29	7.70	7.29	8.64	
$[Rh(NBD)\{(In)_2PyCH\}]$-$[RhCl_2(NBD)]$[b]	8.35	7.67	7.20	7.67	9.42	9.81	8.49	8.02	7.38	9.70	CH_2-7: 1.44; 1.17 CH-2,3,5,6: 3.76; 3.51 CH-1,4: 3.93
	(+0.25)	(−0.04)	(+0.06)	(+0.36)	(+1.92)	(+1.35)	(+1.20)	(+0.32)	(+0.09)	(+1.06)	
$[Rh(NBD)\{(In)_2PyCH\}]Cl$[b]	8.35	7.68	7.22	7.68	9.64	10.22	8.52	7.98	7.41	9.87	CH_2-7: 1.23 CH-2,3,5,6: 3.52 CH-1,4: 3.93
	(+0.25)	(−0.03)	(+0.08)	(+0.37)	(+2.14)	(+1.76)	(+1.23)	(+0.28)	(+0.12)	(+1.23)	

[a] Coupling constants values are in the normal range and are omitted. [b] In $CDCl_3$. [c] In DMSO-d_6. [d] H_{meta}, H_{para}. [e] H_4, H_5, H_6.

Table 7. ^{13}C NMR Data of Ligands (L) and Their Rhodium Complexes Obtained in Acetone, in $CDCl_3$ (Coordination-Induced Shifts (CIS) in Parentheses)

compd	C_3	C_{3a}	C_4	C_5	C_6	C_7	C_{7a}	C(sp^3)	C_{ipso}	C_{ortho}	C_{meta}	C_{para}	NBD carbons[a]
$(Pz)_2CH_2$	140.5		106.9	129.5				65.0					
$[\{RhCl(NBD)\}_2\{(Pz)_2CH_2\}]$	140.8		106.8	135.8				63.2					C_7: 61.5 $C_{2,3,5,6}$: 54.7 $C_{1,4}$: 50.4
	(+0.3)		(−0.1)	(+6.3)				(−1.8)					
$(Pz)_2PhCH$	140.7		106.5	129.6				77.7	136.1	128.8	126.9	129.2	
$[\{RhCl(NBD)\}_2\{(Pz)_2PhCH\}]$	141.0		106.6	136.7				74.6	137.0	125.9	128.5	129.3	C_7: 61.3 $C_{2,3,5,6}$: 58.5 $C_{1,4}$: 50.0
	(+0.3)		(+0.1)	(+7.1)				(−3.1)	(+0.9)	(−2.9)	(+1.6)	(+0.1)	
$[RhCl(NBD)\{(Pz)_2PhCH\}]$	141.1		106.7	135.4				74.5	136.7	125.8	128.6	129.3	C_7: 61.8; J_{Rh} = 2.7 $C_{2,3,5,6}$: 57.3 $C_{1,4}$: 50.6; J_{Rh} = 6.2
	(+0.4)		(+0.2)	(+5.8)				(−3.2)	(+0.6)	(−3.0)	(+1.7)	(+0.1)	
$(In)_2PhCH$	134.8	124.9	121.5	121.0	126.8	110.9	139.9	74.8	135.2	128.5	127.5	128.8	
$[Rh(NBD)\{(In)_2PhCH\}][RhCl_2(NBD)]$	135.4[a]	123.7[a]	122.2[a]	120.8	*b*	111.4	140.2	73.6	135.9	127.2	128.7	129.1	C_7: 60.5 $C_{2,3,5,6}$: 50.6 $C_{1,4}$: 49.9
	(+0.6)	(−1.2)	(+0.7)	(−0.2)		(+0.5)	(+0.3)	(−1.2)	(+0.7)	(−1.3)	(+1.2)	(+0.3)	
$(Pz)_3CH$	141.7		107.2	129.4				83.2					
$[Rh(NBD)\{(Pz)_3CH\}][RhCl_2(NBD)]$	141.9		107.0	133.8				74.3					C_7: 58.4 $C_{2,3,5,6}$: 38.4 $C_{1,4}$: 47.9
	(+0.2)		(−0.2)	(+4.4)				(−8.9)					
$[Rh(NBD)\{(Pz)_3CH\}]Cl$	141.9		107.1	133.3				73.9					C_7: 58.6 $C_{2,3,5,6}$: 38.6 $C_{1,4}$: 48.0
	(+0.2)		(−0.1)	(+3.9)				(−9.3)					

[a] Broad signals. [b] Not detected.

the rhodium atom, the two nitrogen atoms of the pyrazole rings, and the centroids G1 and G2 of the double bonds of the NBD ligand. As in the case of its aforementioned hexafluorophosphate analogue, the metallocycle Rh-(NN)$_2$Cl also exists in a boat conformation (Figure 2).

Taking into account that these ion-pair structures usually give nonequivalent resonances in ^{1}H NMR spectra for the two different NBD groups, the $[Rh(NBD)\{(Pz)_2PhCH\}][RhCl_2(NBD)]$ behaves anomalously. The NBD protons appear as three broad singlets at δ = 4.19, 3.75, and 1.24 ppm (see Table 6). This feature suggests that the complex presents in solution the equilibrium indicated in Scheme 1. The same explanation could be applied for the complex $[\{RhCl(NBD)\}_2\{(Pz)_2CH_2\}]$. Also, ^{13}C NMR data would confirm this equilibrium considering the broad resonances observed primarily in the NBD signals (see

Table 8. Selected Bond Lengths (Å) and Bond Angles (deg) of the Complex [Rh(NBD){(Pz)$_2$PhCH}][RhCl$_2$(NBD)] (with Esd's)

	Bond Lengths		
Rh1–N11	2.089(4)	C31–C32	1.515(8)
Rh1–N21	2.078(4)	C31–C36	1.384(8)
Rh1–C31	2.109(6)	C32–C33	1.536(9)
Rh1–C33	2.125(5)	C32–C37	1.546(8)
Rh1–C34	2.124(5)	C33–C34	1.401(7)
Rh1–C36	2.101(5)	C34–C35	1.531(8)
Rh2–Cl1	2.409(1)	C35–C36	1.542(7)
Rh2–Cl2	2.380(2)	C35–C37	1.526(9)
Rh2–C41	2.102(5)	C41–C42	1.533(7)
Rh2–C43	2.092(5)	C41–C46	1.389(7)
Rh2–C44	2.088(5)	C42–C43	1.532(7)
Rh2–C46	2.100(5)	C42–C47	1.525(7)
N12–C1	1.455(6)	C43–C44	1.375(7)
N22–C1	1.457(5)	C44–C45	1.532(7)
C1–C2	1.523(6)	C45–C46	1.530(7)
		C45–C47	1.521(8)
Rh1–C2	3.235(5)		
Rh1–C7	3.474(5)		
Rh1–H1	4.22		
Rh1–G1[a]	1.988(6)		
Rh1–G2[a]	2.001(5)		
Rh2–G3[a]	1.983(5)		
Rh2–G4[a]	1.973(5)		
	Bond Angles		
C34–Rh1–C36	67.9(2)	C44–Rh2–C46	67.5(2)
C33–Rh1–C36	80.9(9)	C43–Rh2–C46	80.5(2)
C33–Rh1–C34	38.5(2)	C43–Rh2–C44	38.4(2)
C31–Rh1–C36	38.4(2)	C41–Rh2–C46	38.6(2)
C31–Rh1–C34	80.8(2)	C41–Rh2–C44	80.4(2)
C31–Rh1–C33	68.0(2)	C41–Rh2–C43	67.4(2)
N21–Rh1–C36	98.4(2)	Cl2–Rh2–C46	160.3(2)
N21–Rh1–C34	158.5(2)	Cl2–Rh2–C44	96.4(2)
N21–Rh1–C33	159.7(2)	Cl2–Rh2–C43	93.9(1)
N21–Rh1–C31	98.8(2)	Cl2–Rh2–C41	153.9(1)
N11–Rh1–C36	155.4(2)	Cl1–Rh2–C46	97.3(1)
N11–Rh1–C34	98.0(2)	Cl1–Rh2–C44	157.3(1)
N11–Rh1–C33	100.8(2)	Cl1–Rh2–C43	159.9(2)
N11–Rh1–C31	163.5(2)	Cl1–Rh2–C41	98.4(2)
N11–Rh1–N22	88.3(2)	Cl1–Rh2–Cl2	94.2(2)
		N12–C1–N22	109.7(3)
		H1–C1–N22	109.3(4)
		H1–C1–N12	107.7(4)
		N22–C1–C2	110.7(4)
		N12–C1–C2	111.9(3)
		H1–C1–C2	107.5(4)

[a] G1 = centroid (C31–C36), G2 = centroid (C33–C34), G3 = centroid (C41–C46), G4 = centroid (C43–C44).

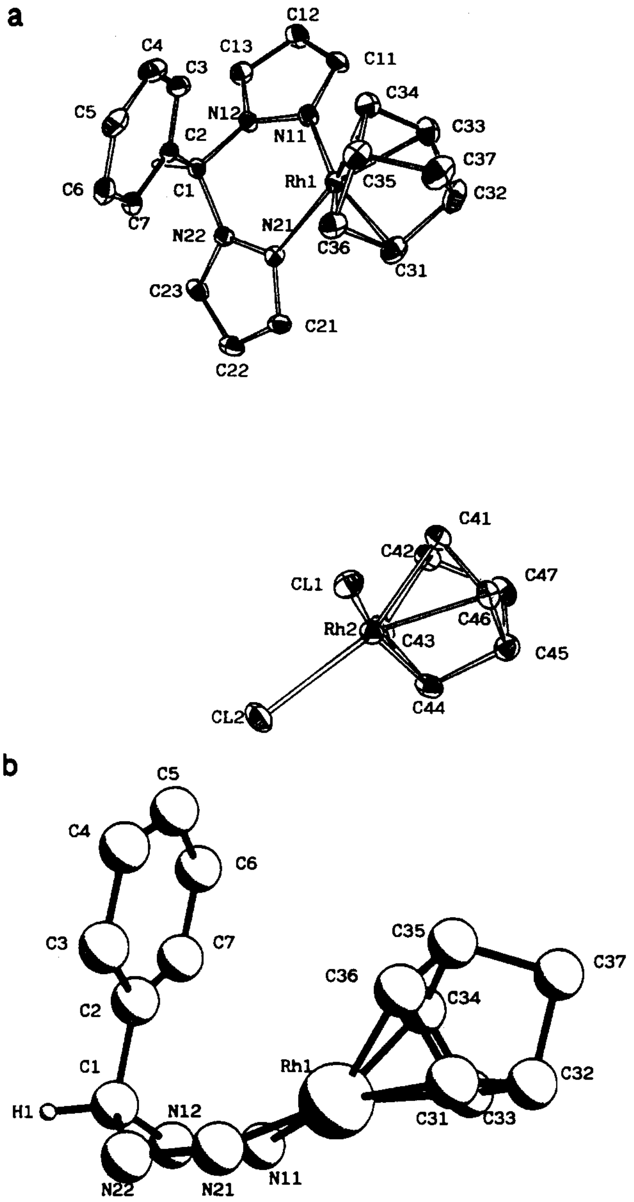

Figure 2. (a) Perspective ORTEP[18] view of [Rh(NBD){(Pz)$_2$PhCH}][RhCl$_2$(NBD)] with atomic numbering scheme. H atoms are omitted, and thermal ellipsoids are at the 70% probability level. (b) A PLUTO plot of the Rh1N11N12C1N21N22 metallocycle. Pyrazole carbons are omitted for clarity.

Table 7) which reveal a detectable chemical exchange. Although the mechanism of chloride ion transfer is not clearly established, similar equilibria have recently been reported for rhodium(I) complexes with aliphatic and aromatic diamines involving intermediate dinuclear species.[17]

The ligand (In)$_2$PhCH yielded, in both molar ratios, the same kind of complex. Considering the analytical data and especially the ^{1}H NMR spectrum (Tables 5 and 6), also an ion-pair structure [Rh(NBD){(In)$_2$PhCH}][RhCl$_2$(NBD)] can be assigned. NBD protons gave six different resonances (see Table 6) which correspond to two types of NBD ligands of the complex.

The tridentate ligand (In)$_2$PyCH gave, in a 1:1 molar ratio, a pentacoordinate ion pair complex [Rh(NBD){(In)$_2$PyCH}][RhCl$_2$(NBD)]. Also in this case the two types of NBD protons are detected in the ^{1}H NMR spectrum (Table 6). The cationic species of this complex should be analogous to that previously described for the related [Rh(NBD){(In)$_2$PyCH}]PF$_6$.[5] (NNN)Rh(NBD) pentacoordination is also observed in the ^{1}H NMR spectrum, but due to the presence of two types of NBD ligands in the ion-pair complex, the NBD protons give an overlapped system at δ = 3.93, 3.76, and 3.51 ppm (6:2:4) for olefinic and methinic protons. A similar ion-pair complex [Rh(NBD){(Pz)$_3$CH}][RhCl$_2$(NBD)] was obtained when (Pz)$_3$CH was used as ligand.[19]

When (Pz)$_2$PhCH and (In)$_2$PyCH reacted in actone in a dimer:ligand molar ratio of 1:2, yellow solids were isolated. Their analytical data correspond to the formulas [RhCl(NBD){(Pz)$_2$PhCH}] and [Rh(NBD){(In)$_2$PyCH}]Cl. IR

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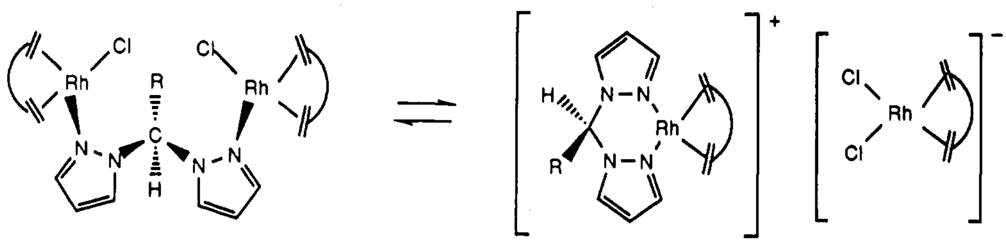
(19) Results from ref 4 and this work.

Scheme 1. Proposed Equilibrium in Solution for Complexes of $(Pz)_2CH_2$ and $(Pz)_2PhCH$ Obtained in Acetone, 1:1



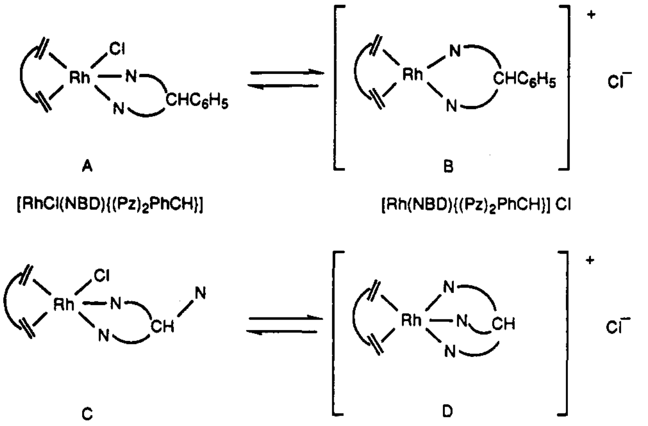
$[\{RhCl(NBD)\}_2\{(Pz)_2CH_2\}]$ R = H

$[\{RhCl(NBD)\}_2\{(Pz)_2PhCH\}]$ R = C_6H_5

$[Rh(NBD)\{(Pz)_2CH_2\}][RhCl_2(NBD)]$ R = H

$[Rh(NBD)\{(Pz)_2PhCH\}][RhCl_2(NBD)]$ R = C_6H_5

Scheme 2. Proposed Equilibrium in Solution for Complexes of $(Pz)_2PhCH$, $(In)_2PyCH$, and $(Pz)_3CH$ in Acetone, 1:2



$[RhCl(NBD)\{(Pz)_2PhCH\}]$

$[Rh(NBD)\{(Pz)_2PhCH\}]\,Cl$

$[RhCl(NBD)\{(In_2)PyCH\}]$
$[RhCl(NBD)\{(Pz)_3CH\}]$

$[Rh(NBD)\{(In_2)PyCH\}]\,Cl$
$[Rh(NBD)\{(Pz)_3CH\}]\,Cl$

and ^1H and ^{13}C NMR spectroscopic data (Tables 5–7) revealed pentacoordination around the rhodium atom. Similar coordination of the pyrazole ring has been described previously.[2] According to the NMR data we can infer that the structure of the complexes in solution would mainly correspond to the neutral A form in the $(Pz)_2PhCH$ derivative and the cationic D form in the $(In)_2PyCH$ derivative (Scheme 2). The latter form was previously reported for the complex from $(Pz)_3CH_4$ and confirmed in this work. These equilibria are the consequence of the nucleophilic attack of the chloride ion on the rhodium metal in the cationic species. In $(Pz)_2PhCH$ the tetracoordinate cationic form would yield the pentacoordinate neutral complex, and in $(In)_2PyCH$ and $(Pz)_3CH$ the substitution of one pyrazole by a chloride would afford C. Such behavior does not occur in the case of the PF_6 counterion due to its lower nucleophilic character. The analogous tris(pyrazolyl)borate complexes [Rh(diolefin){$(Pz)_3BH$}] (diolefin = duroquinone, COD, and NBD) undergo a similar type of exchange.[20]

Concluding Remarks

The five polyazolylmethanes used in this study are very effective ligands for rhodium(I). The general tendency of all of them is to yield tetra- or pentacoordinate cationic species which can be irreversibly trapped in methanol solution as PF_6 salts. The ion-pair structures obtained in actone 1:1 seem to be the unique species in the solid state as proved by the X-ray results of the complex derived from $(Pz)_2PhCH$. However, in solution, the ion-pair species from pyrazole derivatives are equilibrated with neutral forms. Indazole tetracoordinate complexes and all pentacoordinate complexes exist in solution mainly as cationic species.

We have established that ^1H and ^{13}C NMR spectroscopies are useful tools to deduce the coordination of the ligands by analysis of the NBD resonances.

Experimental Section

NMR data were acquired at 25 °C. ^1H spectra were performed on a Varian XL-300 (299.95 MHz), and ^{13}C spectra were recorded on a Bruker AC-200 (50.33 MHz) spectrometer. Chemical shifts are listed in parts per million relative to tetramethylsilane, and coupling constants are in hertz. The ^1H and ^{13}C chemical shifts are accurate to 0.01 and 0.1 ppm, respectively. Coupling constants are accurate to ±0.2 Hz for ^1H NMR spectra and ±0.6 Hz for ^{13}C NMR spectra. DEPT sequences were carried out in the usual manner.[21] IR spectra were recorded on a Perkin-Elmer 1300 spectrometer, and the conductivity was measured at 20 °C with a Phillips PR 9500 conductometer with a PR9512/00 cell. Commercial solvents were dried prior to use. Syntheses of the ligands have been described previously: $(Pz)_2CH_2$,[22] $(Pz)_2PhCH$,[23] $(In)_2PhCH$,[24] $(Pz)_3CH$,[25] and $(In)_2PyCH$.[5]

Reaction of the Ligands with $[RhCl(NBD)]_2$ in Methanol. To a suspension of $[RhCl(NBD)]_2$ (0.1 mmol) in methanol (15 mL) was added ligand (0.2 mmol). The clear yellow solution that formed immediately after the addition was stirred at room temperature for 1 h. Then KPF_6 (0.2 mmol) was added, and the resulting solution was stirred for 20 min and evaporated *in vacuo* to approximately 5 mL. The concentrated solution was kept at 0 °C for 24 h, and a yellow solid crystallized, which was filtered off and dried. Yields are given in Table 1.

Reactions of the Ligands with $[RhCl(NBD)]_2$ in Acetone. To a yellow solution of $[RhCl(NBD)]_2$ (0.1 mmol) in acetone (10 mL) was added ligand (0.1 mmol or 0.2 mmol). The solution was stirred at room temperature for 1 h. Then the volume was reduced *in vacuo* to approximately 2 mL. The formed orange or yellow crystalline solid was filtered off, washed with small portions of acetone, and dried *in vacuo*. Yields are given in Table 5.

X-ray Structure Determination. Single yellow and prismatic crystals of [Rh(NBD){$(Pz)_2PhCH$}]PF_6 and [Rh-

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Table 9. Crystal and Refinement Data for $[Rh(NBD)\{(Pz)_2PhCH\}]PF_6$ (I) and $[Rh(NBD)\{(Pz)_2PhCH\}][RhCl_2(NBD)]$ (II)

	I	II
formula	$C_{20}H_{20}N_4RhPF_6$	$C_{27}H_{28}N_4Rh_2Cl_2$
M_r	564.27	685.26
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
a, Å	14.87(1)	12.500(1)
b, Å	12.02(2)	9.790(3)
c, Å	12.325(4)	21.261(5)
β, deg	94.24(5)	98.05(2)
V, Å^3	2196(4)	2576(1)
Z	4	4
F(000)	1228	1368
ρ(calcd), g cm^{-3}	1.70	1.77
temp, K	294	294
μ, cm^{-1}	8.9	15.0
cryst dimens, mm	0.5 × 0.2 × 0.2	0.4 × 0.3 × 0.4
diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4
radiation	graphite-monochromated Mo Kα (λ = 0.710 69 Å)	graphite-monochromated Mo Kα (λ = 0.710 69 Å)
scan technique	$\Omega/2\theta$	$\Omega/2\theta$
data collected	(–17,0,0)–(17,14,14)	(–14,0,0)–(14,11,25)
θ	$1 < \theta < 25$	$1 < \theta < 25$
no. of unique data	3867	4515
no. of unique data $I \geq 2\sigma(I)$	1647	3394
std rflns	3/128	3/195
R(int) (%)	1.7	0.7
R_F, %	9.4	2.6
R_{wF}, %	10.6	3.2
average shift/error	0.29	0.07

Table 10. Atomic Coordinates and Thermal Parameters for Non-Hydrogen Atoms of $[Rh(NBD)\{(Pz)_2PhCH\}]PF_6$

atom	x/a	y/b	z/c	U_{eq},^{a} Å^2
Rh	0.6944(1)	0.3830(2)	0.3699(2)	490(6)
P	0.7929(4)	0.6125(8)	–0.2369(5)	582(23)
F1	0.7154(15)	0.6560(19)	–0.1679(18)	1396(76)
F2	0.7318(14)	0.6393(19)	–0.3440(17)	1344(72)
F3	0.8655(15)	0.5628(19)	–0.3058(18)	1357(75)
F4	0.8492(16)	0.5825(20)	–0.1349(19)	1506(86)
F5	0.7562(25)	0.4938(33)	–0.2361(29)	2271(123)
F6	0.8271(22)	0.7277(30)	–0.2471(26)	2144(111)
N11	0.5931(16)	0.5018(19)	0.3709(18)	605(93)
N12	0.5124(14)	0.4915(17)	0.3240(17)	476(80)
N21	0.5889(14)	0.2662(18)	0.3616(19)	577(87)
N22	0.5089(16)	0.2874(17)	0.3214(17)	543(87)
C1	0.4957(15)	0.3939(22)	0.2544(20)	555(89)
C2	0.5521(15)	0.3907(24)	0.1583(16)	480(78)
C3	0.5712(21)	0.2900(23)	0.1091(24)	646(116)
C4	0.6224(24)	0.2916(29)	0.0157(24)	814(139)
C5	0.6553(21)	0.3861(33)	–0.0222(21)	829(119)
C6	0.6330(25)	0.4840(29)	0.0287(25)	824(144)
C7	0.5834(21)	0.4865(23)	0.1155(25)	702(124)
C11	0.5948(17)	0.6058(23)	0.4189(19)	574(91)
C12	0.5075(23)	0.6530(28)	0.3935(24)	832(132)
C13	0.4575(22)	0.5746(26)	0.3362(24)	708(130)
C21	0.5872(20)	0.1647(25)	0.3933(19)	637(106)
C22	0.4972(21)	0.1228(34)	0.3724(23)	831(126)
C23	0.4512(22)	0.2053(28)	0.3252(25)	705(125)
C31	0.8011(18)	0.4784(21)	0.3225(29)	617(116)
C32	0.8587(22)	0.3790(38)	0.2822(31)	1213(171)
C33	0.8014(20)	0.2920(22)	0.3145(30)	703(128)
C34	0.8043(21)	0.2842(25)	0.4249(28)	759(138)
C35	0.8649(21)	0.3746(32)	0.4687(28)	967(138)
C36	0.8027(18)	0.4785(22)	0.4307(30)	706(132)
C37	0.9333(21)	0.3715(42)	0.3751(31)	1247(182)

^{a} $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\mathbf{a}_j \times 10^4$

$(NBD)\{(Pz)_2PhCH\}][RhCl_2(NBD)]$ were obtained from methanol and acetone, respectively. The data were collected on an Enraf-Nonius CAD-4 diffractometer for both compounds, and unit cell constants were refined from least-squares fitting of the the θ values of 25 reflections. A summary of the fundamental crystal data is given in Table 9.

The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Rh, P, and Cl were taken from ref 26. Both structures were solved by Patterson and Fourier methods.

Table 11. Atomic Coordinates and Thermal Parameters for Non-Hydrogen Atoms of $[Rh(NBD)\{(Pz)_2PhCH\}][RhCl_2(NBD)]$

atom	x/a	y/b	z/c	U_{eq},^{a} Å^2
Rh1	0.216 57(3)	0.001 90(4)	0.574 01(2)	374(1)
Rh2	0.361 87(3)	0.114 40(4)	0.172 51(2)	379(1)
Cl1	0.553 32(9)	0.090 53(13)	0.205 82(6)	507(4)
Cl2	0.351 30(11)	–0.076 78(14)	0.102 85(6)	613(5)
N11	0.141 62(29)	–0.066 48(37)	0.650 00(17)	390(12)
N12	0.099 46(28)	–0.194 49(36)	0.649 91(17)	362(12)
N21	0.113 87(28)	–0.124 85(38)	0.514 89(17)	390(12)
N22	0.067 57(27)	–0.235 88(36)	0.538 51(16)	360(12)
C1	0.115 43(34)	–0.290 46(43)	0.599 79(20)	355(14)
C2	0.234 43(34)	–0.323 42(42)	0.599 60(20)	348(13)
C3	0.266 16(36)	–0.381 21(47)	0.545 50(21)	412(15)
C4	0.374 09(41)	–0.409 77(50)	0.543 96(24)	505(18)
C5	0.450 47(38)	–0.380 54(56)	0.596 36(27)	551(18)
C6	0.417 76(41)	–0.325 95(60)	0.649 83(25)	577(19)
C7	0.310 95(37)	–0.297 30(50)	0.651 93(22)	448(16)
C11	0.127 91(39)	–0.013 77(52)	0.705 97(22)	482(16)
C12	0.078 12(44)	–0.105 69(58)	0.741 28(23)	563(19)
C13	0.061 61(40)	–0.220 51(52)	0.704 87(23)	486(17)
C21	0.068 00(36)	–0.115 03(52)	0.454 30(20)	436(15)
C22	–0.004 89(38)	–0.220 30(57)	0.438 88(22)	506(17)
C23	–0.002 36(36)	–0.296 14(49)	0.492 87(24)	448(15)
C31	0.272 81(40)	0.124 78(57)	0.504 05(25)	570(19)
C32	0.314 62(44)	0.239 33(55)	0.548 69(31)	658(22)
C33	0.291 40(39)	0.183 77(53)	0.613 04(27)	543(19)
C34	0.362 28(39)	0.073 70(52)	0.627 08(24)	500(17)
C35	0.429 31(40)	0.064 96(57)	0.572 22(27)	569(19)
C36	0.342 45(40)	0.015 84(58)	0.518 33(24)	549(19)
C37	0.437 86(47)	0.215 36(67)	0.554 74(32)	760(25)
C41	0.323 00(37)	0.223 45(51)	0.251 44(22)	452(16)
C42	0.200 83(38)	0.198 31(53)	0.238 78(23)	480(17)
C43	0.195 80(35)	0.117 03(53)	0.176 88(24)	489(17)
C44	0.218 89(38)	0.207 48(55)	0.131 23(23)	488(17)
C45	0.238 42(40)	0.345 95(52)	0.164 38(24)	508(18)
C46	0.346 39(38)	0.314 79(48)	0.205 23(24)	464(16)
C47	0.159 96(40)	0.336 94(55)	0.212 92(25)	556(19)

^{a} $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\mathbf{a}_j \times 10^4$.

Empirical absorption corrections[27] were applied at the end of the isotropic refinements. The maximum and minimum absorption

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(26) *International Tables for X-ray Crystallography*, Kynoch Press: Birmingham, 1974; Vol 4, pp 72–98.

(27) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158.

correction factors were 1.115 and 0.987 for $[Rh(NBD)\{(Pz)_2PhCH\}]PF_6$ and 1.123 and 0.929 for $[Rh(NBD)\{(Pz)_2PhCH\}][RhCl_2(NBD)]$.

For $[Rh(NBD)\{(Pz)_2PhCH\}]PF_6$ some nonresolvable disorder from the thermal motion has been found for the F atoms of PF_6. For this reason, these atoms have been refined only isotropically. Final mixed refinement with unit weight = 2 and coordinates for hydrogen atoms converged at $R = 9.4$. For $[Rh(NBD)\{(Pz)_2PhCH\}][RhCl_2(NBD)]$ final mixed refinement with unit weight employed fixed coordinates and isotropic thermal factors for the hydrogen atoms led to $R = 2.6$. Calculations were performed using the X-ray 80 program.[28] No trends in ΔF vs F_o or $(\sin \theta)/\lambda$ were observed.

Refined atomic coordinates for $[Rh(NBD)\{(Pz)_2PhCH\}]PF_6$ and $[Rh(NBD)\{(Pz)_2PhCH\}][RhCl_2(NBD)]$ are given in Tables 10 and 11, respectively.

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Supplementary Material Available: Tables giving fractional coordinates, thermal parameters, and bond distances and angles for $[Rh(NBD)\{(Pz)_2Ph\}]PF_6$ and $[Rh(NBD)\{(Pz)_2PhCH\}][RhCl_2(NBD)]$ (16 pages). Ordering information is given on any current masthead page. Tables of observed and calculated structure factors for $[Rh(NBD)\{(Pz)_2PhCH\}]PF_6$ and $[Rh(NBD)\{Pz)_2PhCH\}][RhCl_2(NBD)]$ can be obtained from the authors.

OM930385C

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[28] Stewart, J. M. *The X-ray 80 System*; Computer Science Centre University of Maryland: College Park, MD, 1985.