Journal of Organometallic Chemistry, 219 (1981) 409—420
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

THE PREPARATION AND REACTIONS OF BIS(PYRAZOLYL)PHENYLMETHANE COMPLEXES OF RHODIUM(I)

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(Received February 12th, 1981)

Summary

The complexes $[(LL)Rh(C_2H_4)Cl]_x$ (I), $[(LL)(Rh(cod)Cl)_2]$ (II), $[(MeLL)Rh(C_2H_4)_2Cl]$ (III) and $[(MeLL)Rh(cod)]^+Cl^-$ (IV) have been prepared via the reactions of the bis-(pyrazolyl)phenylmethane ligands $PhCH(H_2pz)_2$ (LL; H_2pz = pyrazolyl) and $PhCH(Me_2pz)_2$ (MeLL; Me_2pz = 3,5-dimethylpyrazolyl) with $[Rh(C_2H_4)_2Cl]_2$ and $[Rh(cod)Cl]_2$ (cod = cyclooctadiene). Complex IV reacts with $NaBPh_4$ to form $[(MeLL)Rh(cod)]^+BPh_4^-$ (V). III and IV react with carbon monoxide to give $[(MeLL)Rh(CO)_2]^+[Rh(CO)_2Cl_2]^-$ (VI). Complexes I and III give neutral solutions in methanol, while II and IV behave as 1 : 2 and 1 : 1 electrolytes, respectively. The rhodium(I) centre is typically four-coordinate in I, II, IV—VI, and five-coordinate in III. The ligands LL and MeLL show bidentate chelating behaviour in all of the above complexes, with the exception of II, where LL bridges two different Rh^I moieties. Reactions with H_2, HCl and Ph_3P are described. Complex III functions as a homogeneous catalyst, in neutral methanolic solution, for the hydrogenation of olefins, but is ineffective for the hydrogenation of α,β-unsaturated aldehydes and ketones.

Introduction

In many homogeneous catalytic processes, coordinatively unsaturated species play an important role [1—4]. We have found that bis(pyrazolyl)phenylphosphine [5—7] and structurally related bis-(pyrazolyl)phenylmethane [8] ligands give rise to coordinatively unsaturated complexes of Group VI carbonyls, viz. $[E(Me_2pz)_2M(CO)_3]$ (E = PhP or PhCH; M = Mo, W). The sixth coordination site is blocked by the phenyl substituent on the ligand [9]. We now report the reactions of the ligands $PhCH(R_2pz)_2$ with $[Rh(C_2H_4)_2Cl]_2$ [10] and $[Rh(cod)Cl]_2$ [11] (cod = cyclooctadiene) as possible routes to formally three-coordinate Rh^I species with structures stabilized by a M - - -(phenyl) interaction analogous to that observed in $[PhP(Me_2pz)_2W(CO)_3]$ [9]. Three coordination ostensibly occurs in $[Rh(PPh_3)_3]^+$ [12] and in $[RhX(P(C_6H_{11})_3)_2]$ [13a], and the concept has been the subject of a review article [13b].

Rhodium(I) complexes of related pyrazolylborate ligands [14,15], and the biological activity of N-heterocycle complexes of rhodium [16] have been described in the literature.

Discussion

The bis(pyrazolyl)phenylmethane ligands $PhCH(R_2pz)_2$, containing two pyridine-like N-donor centres, are potentially capable of chelating (Fig. 1a) and bridging (Fig. 1b) bidentate coordination modes, as well as monodentate behaviour. The analytical data and macroscopic properties, the ^1H NMR data, and the ^{13}C NMR data for the ligands and their Rh^I complexes are collected in Tables 1—3, respectively.

The reaction of $PhCH(H_2pz)_2(LL)$ with $[Rh(C_2H_4)_2Cl]_2$ in a 2 : 1 molar ratio under mild conditions in benzene results in the displacement of half of the ethylene, and formation of yellow $[(LL)Rh(C_2H_4)Cl]_x$ (I). Complex I is relatively insoluble in most common organic solvents, and is unstable in CS_2 and in halogenated solvents. Conductivity measurements showed that I is very weakly dissociated in methanol (Λ_M = 26 ohm^{-1} mole^{-1} l) [17], and it does not react with aqueous/methanolic $NaBPh_4$. The ^1H NMR spectrum of I in DMSO-d_6 indicated that the H_2pz rings are equivalent. Possible structures for I include a

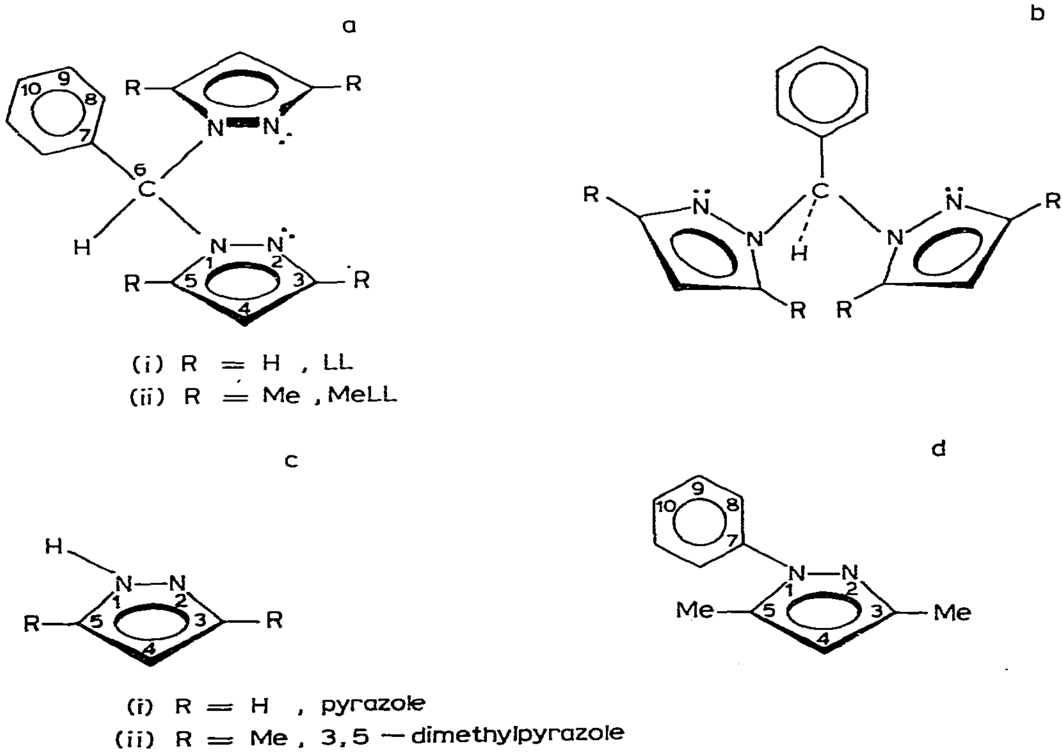

Fig. 1. Structures and numbering schemes for pyrazolyl ligands.

TABLE 1

RHODIUM(I) COMPLEXES OF BIS(PYRAZOLYL)PHENYLMETHANES [a,b]

	Compound	M. Pt. (°C)	Yield (%)	Λ_M [c]	Analyses. Found (calcd.) (%)		
					C	H	N
	MeLL	66—67	62	—	72.8 (72.80)	7.17 (7.20)	20.0 (20.00)
I	$[(LL)Rh(C_2H_4)Cl]$	155 (dec)	92	26	45.5 (46.08)	4.04 (4.13)	13.8 (13.34)
II	$[(LL)(Rh(cod)Cl)_2]$	175	76	150	48.8 (48.52)	5.14 (5.06)	7.83 (7.81)
III	$[(MeLL)Rh(C_2H_4)_2Cl]$ [d]	105—107	65	39	53.4 (53.08)	6.10 (5.95)	11.9 (11.80)
IV	$[(MeLL)Rh(cod)]Cl$ [e]	147	77	77	55.7 (56.95)	5.90 (6.12)	10.1 (10.64)
V	$[(MeLL)Rh(cod)2BPh_4$	—	49	—	72.5 (72.56)	6.55 (6.50)	6.79 (6.91)
VI	$[(MeLL)Rh(CO)_2]^+$ $[Rh(CO)_2Cl_2]^-$	137 (dec)	50	—	38.9 (37.67)	3.11 (3.01)	8.47 (8.38)

[a] LL = $PhCH(H_2pz)_2$ = bis(pyrazolyl)phenylmethane; MeLL = $PhCH(Me_2pz)_2$ = bis(3,5-dimethylpyrazolyl)-phenylmethane. [b] Colours: MeLL, white; I—IV, yellow; V, pale yellow. [c] Molar conductance, in ohm^{-1} mol^{-1} l; in methanol. [d] $M_{calcd.}$ = 474.7; M_{found} = 394, in methanol. [e] $M_{calcd.}$ = 526.7; M_{found} = 271, in methanol.

mononuclear configuration involving chelating LL (Fig. 2a) and a halogen-bridged dimeric structure in which LL is monodentate (Fig. 2b).

The reaction of LL with $[Rh(cod)Cl]_2$ (1 : 1 molar ratio; cod = cyclooctadiene) gave $[(LL)(Rh(cod)Cl)_2]$ (II).

Possible formulations for II include an LL-bridged species $[(cod)Rh(Cl)(\mu\text{-}LL)Rh(Cl)(cod)]$ (IIa), mono- and di-cationic forms of IIa, and the ion pair $[(LL)Rh(cod)]^+[Rh(cod)Cl_2]^-$ (IIb), in which LL is a chelating ligand.

Complex II is slightly soluble in methanol, in which its molar conductance (150 ohm^{-1} $mole^{-1}$ l) lies at the lower limit for a 1 : 2 electrolyte [17]. The

TABLE 2

^{1}H NMR DATA FOR RHODIUM(I) COMPLEXES OF BIS-(PYRAZOLYL)PHENYLMETHANES [a]

	Compound [b, c]	6-CH	3-R	5-R	4-H	olefinic H
	MeLL	2.37(s)	7.79(s)	7.81(s)	4.15(s)	—
I	$[(LL)Rh(C_2H_4)Cl]$	1.9(b)	2.1(b)	2.4(d)	3.6(b)	6.3(b)
II	$[(LL)(Rh(cod)Cl)_2]$ [d]	1.53(s)	1.61(d)	2.81(d) [e]	3.37(t) [e]	5.9(v. br)
III	$[(MeLL)Rh(C_2H_4)_2Cl]$	2.08(s)	7.24(s)	7.43(s)	3.57(s)	6.98(d) [f]
IV	$[(MeLL)Rh(cod)]Cl$ [d]	2.06(s)	7.49(s)	7.57(s)	3.80(s)	5.79(br)

[a] Data is given in τ values, relative to internal TMS, τ = 10 ppm. s = singlet, d = doublet, m = multiplet, t = triplet; br = broad. The five protons of the phenyl ring were observed as two sets of multiplets: MeLL, 2.65—2.75 and 3.04—3.12; I, 2.60 (centre) and 2.93 (centre); II, 2.37—2.71; III, 2.10—2.13 and 2.50—2.55; IV, 2.25—2.33 and 2.38—2.97. The phenyl, 3-H and 5-H protons of LL gave an overlapping multiplet, 2.29—3.05; 4-H was at 3.72(t) (J = 2.4 Hz). [b] The solvents were: MeLL, $CDCl_3$; I, DMSO-d_6; II, III and IV, CD_3OD. [c] For numbering scheme, see Figs. 1a—1d; R = H in LL; R = Me in MeLL. [d] The methylene resonances of cod were two sets of multiplets, 7.6—8.4, for II; and at 7.7—8.5 for IV. The spectrum of $[Rh(cod)Cl]_2$ in $CDCl_3$ showed τ 5.77 (s, olefinic H), 7.2—7.9 and 8.0—8.7 (methylene multiplets). [e] $J_{3,4} \simeq J_{4,5} \sim 2.5$ Hz. [f] $J(Rh—H) \simeq 0.5$ Hz.

TABLE 3

^{13}C NMR DATA FOR DERIVATIVES OF PYRAZOLE AND RHODIUM(I) COMPLEXES OF BIS-(PYRAZOLYL)PHENYLMETHANES [a]

Carbon atom [b]	LL [c]	MeLL [d]	III	IV	H_2pzH [e]	Me_2pzH [f]	Me_2pzPh [g]
3	130.4	140.8	147.9	148.6	133.3	156.2	127.6
4	107.2	106.6	115.5	112.5	104.5	103.4	96.1
5	141.3	148.1	155.2	157.7	133.3	156.2	129.2
6	78.3	73.8	72.5	73.3	—	—	—
7	136.9	136.7	137.2	139.5	—	—	137.1
8	129.8	128.3	132.7	133.4	—	—	117.6
9	127.6	126.6	129.7	130.5	—	—	112.8
10	129.4	128.1	131.8	133.4	—	—	115.4
3-CH_3	—	13.4	38.6	17.5	—	65.3	2.18
5-CH_3	—	111.7	35.1	13.8	—	65.3	0.91

[a] Data in ppm downfield from TMS. The solvents were: $CDCl_3$ (for LL, MeLL, H_2pzH, Me_2pzH); CH_3OH (for III, IV); neat (Me_2pzPh). Proton-bearing carbons were identified by running off-resonance proton decoupled spectra. The assignments of the (3,5), (3-CH_3, 5-CH_3) and (8, 10) pairs of carbons are based on inductive considerations, but are uncertain because the relative influences of inductive and anosotropic electronic effects are unknown. [b] See figures for numbering scheme. [c] LL = $PhCH(H_2pz)_2$ = bis-(pyrazolyl)-phenylmethane, [d] MeLL = $PhCH(Me_2pz)_2$ = bis(3,5-dimethylpyrazolyl)phenylmethane. [e] H_2pzH = pyrazole. [f] Me_2pzH = 3,5-dimethylpyrazole. [g] Me_2pzPh = 1-phenyl, 3,5-dimethylpyrazole.

absence of a ν(Rh—Cl) band at ~300 cm^{-1} is consistent with an ionic formulation. The reaction of II with aqueous/methanolic $NaBPh_4$ was relatively slow. The ^{1}H NMR spectrum of II in CD_3OD consisted of a set of three resonances

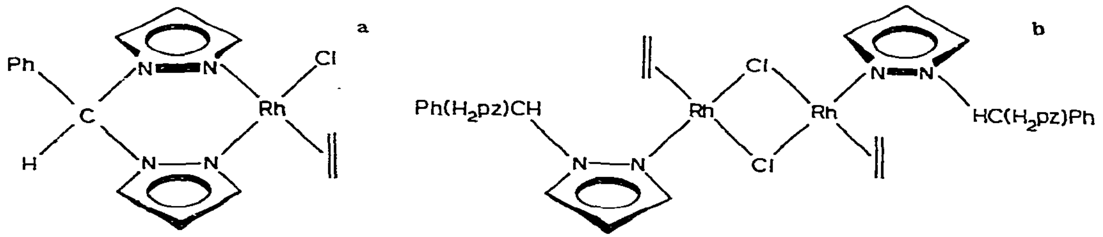

Fig. 2. Possible structures for $[(LL)Rh(C_2H_4)Cl]_x$.

for the two H_2pz rings, thus indicating their equivalence. The 3-H and 5-H resonances (see figures for numbering scheme), just downfield from the phenyl multiplet, were doublets, arising from coupling with 4-H. The 4-H resonance was a triplet, since $J_{3,4} \simeq J_{4,5}$ (~2.5 Hz) [18]. The assignment of the 3- and 5-H resonances cannot be made unambiguously, in the absence of metal—hydrogen coupling constant data [19]. The cod region of the spectrum was similar to that of $[Rh(cod)Cl]_2$, and consisted of two sets of methylene multiplets and a single vinylic resonance. The above data suggests a ligand-bridged structure (Fig. 3), analogous to $[(BB)(Rh(cod)Cl)_2]$ * [20] and related bridged species [21,22]. The alternative uni-univalent ion pair formulation IIb may be discounted because a more complex ^{1}H NMR pattern would be expected for the

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* BB = aminoethylpyridine.

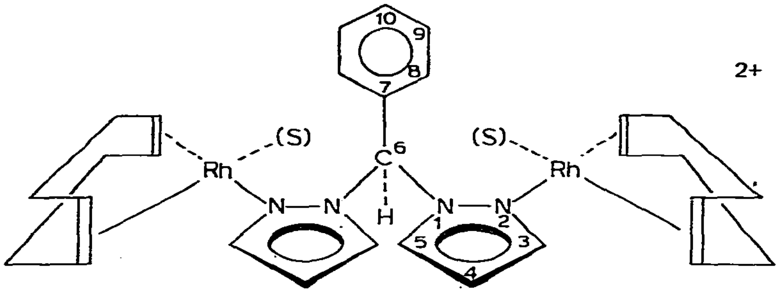

Fig. 3. Possible structure of $[(LL)(Rh(cod))_2]^{2+}$

cod resonances, and the molar conductivity of the bulky ions would be at the lower limit for a 1 : 1 electrolyte [17]. Complexes with the stoichiometry $[(bipy)(Rh(CO)_2Cl)_2]$, analogous to II but with carbonyl ligands replacing the poorer π-accepting diene ligands, have been reported; both bridging [21,23,24] and chelation [25] by the bipyridyl ligand have been claimed for this system.

Reactions between LL and $[Rh(cod)Cl]_2$ in >2 : 1 molar ratios were carried out in an attempt to prepare [(LL)Rh(cod)]Cl, the analogue of IV. Only compound II was produced, however, and excess ligand was recovered. The low solubility of II appears to favour its formation. In a similar fashion, the reaction of bipy with $[Rh(CO)_2Cl_2]^-$ is highly solvent dependent, giving $[(bipy)(Rh(CO)_2Cl)_2]$ in benzene, and [Rh(bipy)(CO)Cl] in acetonitrile.

The reaction of $PhCH(Me_2pz)_2$(MeLL) with $[Rh(C_2H_4)_2Cl]_2$ (2 : 1 molar ratio) gave $[(MeLL)Rh(C_2H_4)_2Cl]$ (III), rather than the mono-ethylene analogue of I. Complex III was monomeric and a weak electrolyte (Λ_M = 39 ohm^{-1} $mole^{-1}$ l) in methanol, and did not react with aqueous methanolic $NaBPh_4$. III was almost insoluble in C_6H_6, and was decomposed by $CHCl_3$, CCl_4 and C_6F_6. The infrared spectrum of III indicated a covalently bound chloro ligand (ν(Rh—Cl) at 300 cm^{-1}, KBr pellet; corresponding literature values are in the 290—310 cm^{-1} range [16,26,27].

The ^1H NMR spectrum of III in CD_3OD showed a singlet 4-H resonance and separate singlet resonances for the 3-Me and 5-Me protons of the two equivalent Me_2pz rings. Similar features occur in the Me_2pz region of the ^1H NMR spectra of [(MeLL)Rh(cod)]Cl (IV) (vide infra) and $[(MeLL)Mo(CO)_4]$ [8]. These observations require chelation by MeLL. The eight ethylene protons of III were observed to be equivalent at room temperature, resonating as a doublet ($J(^{103}Rh—H)$ ~0.5 Hz) some 2.5 ppm upfield from free ethylene. A similar equivalence of the ethylene protons is observed in $[(acac)Rh(C_2H_4)_2]$ at 25°C, and is attributed to rapid rotation of the ethylenes about the metal—olefin bond [28]. At low temperatures (below —50°C), the ethylene protons of III gave two resonances, separated by ~3.2 ppm. Similarly, the complexes $[(acac)Rh(C_2H_4)_2]$ (a 16-e system) and $[(\pi-C_5H_5)Rh(C_2H_4)_2]$ (an 18-e system) exhibit double resonances for ethylenic protons at —50°C, and at 25°C, respectively [28]. The separate signals, attributed to magnetically distinguishable "inner" and "outer" protons of the ethylene moiety, indicate a restriction to rotation about the metal—olefin axis. The remaining low-field resonances of III were attributable to the methylidene and phenyl protons.

^{13}C NMR spectra of III were observed under broad band and off-resonance proton decoupling conditions. The ethylenes gave rise to a doublet ^{13}C reso-

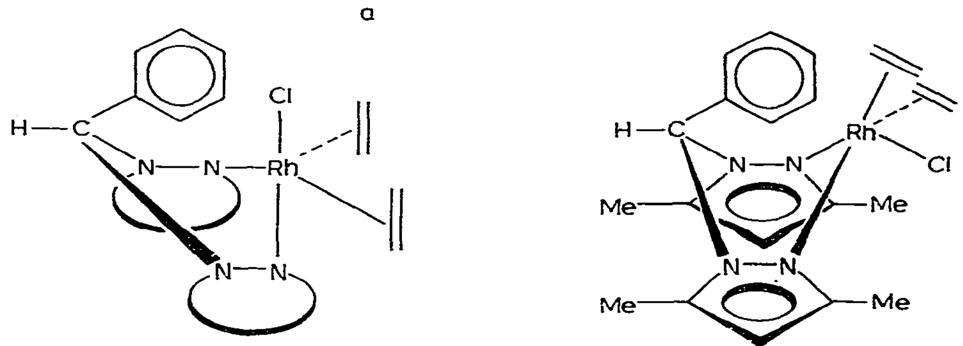

Fig. 4. Possible structures for $[(MeLL)Rh(C_2H_4)_2Cl]$.

nance ($J(^{103}Rh—C)$ = 13 Hz), and the two equivalent Me_2pz rings gave five sets of ^{13}C resonances. Remaining resonances were due to the methylidene and the phenyl carbon atoms.

A study of the possibility of olefin exchange was carried out using a solution of III in CD_3OD containing excess C_2H_4, in a sealed NMR tube. The ^1H NMR doublet resonance for the eight ethylene protons was unchanged, indicating the absence of exchange. This observation, and the spectroscopic data cited above, indicate a coordinately saturated, 18-electron Rh^I complex, rather than a 16-electron system for which facile ligand exchange is usually observed [24,29—31]. Both trigonal bipyramidal (Fig. 4a) and square-based pyramidal (Fig. 4b) geometries for III are consistent with our data *. By contrast, the complexes $[RB(pz)_3Rh(C_2H_4)_2]$ [30,32,33] are 16-electron, four-coordinate systems containing fluxional, dihapto-pyrazolylborate moieties and labile ethylenes.

The reaction of MeLL with $[Rh(cod)Cl]_2$ in a 2 : 1 molar ratio gave $[(MeLL)Rh(cod)]^+Cl^-$ (IV), formulated as the 1 : 1 ionic species in methanol on the basis of conductivity (77.4 ohm^{-1} $mole^{-1}$ l) and fractional solution molecular weight data (M_{obs} = 271 versus $M_{calcd.}$ = 526.7). Infrared evidence confirmed the presence of coordinated MeLL and cod [34], and showed that the typical $\nu(Rh—Cl)$ stretching vibration was absent. In addition, IV reacted readily with $NaBPh_4$ in aqueous methanol to yield $[(MeLL)Rh(cod)]BPh_4$ (V), consistent with the ionic formulation. The two Me_2pz rings of the coordinated MeLL ligand of IV were shown to be equivalent, on the basis of a set of three singlet ^1H resonances for the 3-CH_3, 5-CH_3, and 4-H protons, and a set of five ^{13}C resonances for the 3-CH_3, 3-C, 4-C, 5-C and 5-CH_3 carbon atoms. Under off-resonance decoupling conditions, the methyl carbons and the 4-C appeared as quartets and a doublet, respectively.

The four olefinic protons of cod in IV were equivalent, appearing as a broad singlet, and two sets of methylene ^1H resonances were observed, typical of symmetrically coordinated cod [35]. The proton decoupled ^{13}C spectrum corroborated this interpretation, showing four equivalent methylene carbons as a

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* We thank one of the referees for pointing out that the structures in Figs. 4a and 4b would be expected to give rise to four ^1H resonances for the ethylene protons at low temperatures, corresponding to distinguishable "top" and "bottom" inner and outer protons. Indeed, the individual lines were quite broad, suggestive of this proposed complexity. Unfortunately high field NMR facilities were unavailable for further checking this possibility (see also ref. 31a).

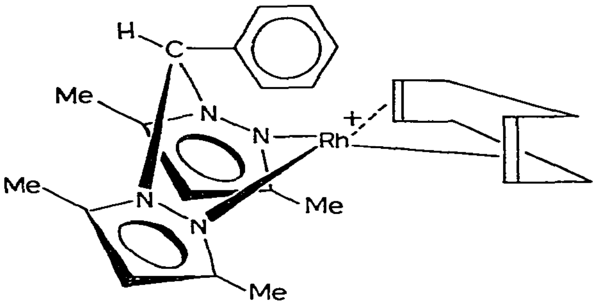

Fig. 5. Possible structure for $[(MeLL)Rh(cod)]^+$

singlet, and four equivalent olefinic carbons as a doublet ($J(^{103}Rh—C) = 13$ Hz; lit. values for $J(^{103}Rh—C)$ in comparable systems are in the range 6—15 Hz [36,37]. The above data indicate a square planar structure for the cationic species in $[(MeLL)Rh(cod)]X$ (X = Cl, BPh_4) (Fig. 5), analogous to reported species of the type $[Rh(N\text{-}N)(diolefin)]^+$ (N-N = bipy, phen) [16,25,38—41]. In the latter systems the metal is constrained within a planar or near-planar five-membered ring system, whereas in IV a six-membered boat metallocyclic $[Rh(N\text{-}N)_2C]$ skeletal structure is expected [42,43] (see Fig. 5).

The reactions of $[Rh(cod)Cl]_2$ with MeLL, bipyridines and *ortho*-phenanthrolines give comparable ionic species $[Rh(N\text{-}N)(cod)]^+$, whereas biquinoline gives neutral, five-coordinate [Rh(biq)(cod)Cl] [27]. A marked difference in colour between IV (yellow) and its bipy and phen analogues [44] (red) is noteworthy. The differences in the structures and bonding at covalent $[(MeLL)Rh(C_2H_4)_2Cl]$ (III) and ionic $[(MeLL)Rh(cod)]^+Cl^-$ (IV) are of interest. Complex III was found to react with cod to give IV, a typical displacement reaction of monoolefin by diolefin [45,46].

The reactions of $[(MeLL)Rh(C_2H_4)_2Cl]$ (III) and [(MeLL)Rh(cod)]Cl (IV) with H_2 and with HCl were examined as possible routes to Rh^{III} oxidative addition products. With molecular H_2, III and IV were reduced relatively slowly to metallic rhodium, IV requiring several hours. The reactivity of $[Rh(N\text{-}N)(olefin)_2]^+$ and $[Rh(N\text{-}N)(diolefin)]^+$ species toward molecular H_2 varies quite widely, depending on the nature of the olefin and the coordinated N-heterocyclic ligands [35,39,41].

The reaction of IV with HCl in methanol and in toluene gave $[Rh(cod)Cl]_2$, identified by its ^1H NMR spectrum. Independent studies have shown that the free ligand MeLL is cleaved by HCl in methanol and toluene [47].

The reactions of III and IV with CO at one atmosphere pressure under mild conditions gave the same compound, viz. $[(MeLL)Rh(CO)_2]^+[Rh(CO)_2Cl_2]^-$ (VI). The yellow colour of VI is in marked contrast to the brilliant greens, reported by Gillard et al. [16], and the red-browns observed by Pruchnik and Wajda [25] for the analogous compounds $[Rh(N\text{-}N)(CO)_2]^+$ $[Rh(CO)_2Cl_2]^-$ (N-N = bipy, phen). The infrared spectra of VI and these analogues are similar, however, over the 2100—1800 cm^{-1} ($\nu(CO)$) region. The reaction of VI with $NaBPh_4$ gave $[(MeLL)Rh(CO)_2]^+BPh_4^-$ (VII) which showed equal intensity strong $\nu(CO)$ bands at 2100 and 2040 cm^{-1}. These two bands, together with absorptions at 2066 and 1982 cm^{-1}, attributable to *cis*-$[Rh(CO)_2Cl_2]^-$ [16,21, 48,49], were observed for VI. The similarity of the corresponding $\nu(CO)$ bands for the dicarbonyl Rh^I cationic complexes of MeLL, bipy, phen and biq

[16,25,27,44,50,51] indicates that the bonding to the metal centre is very similar, or that it is insensitive to structural differences among these systems.

The displacement of olefins and diolefins from 16-electron Rh^I complexes by reaction with CO occurs readily, via an associative mechanism, while 18-electron complexes such as $[(\pi\text{-}C_5H_5)Rh(C_2H_4)_2]$ are comparatively inert to substitution by CO [28,30]. Hence it appears that C_2H_4 in 18-electron $[(MeLL)Rh(C_2H_4)_2Cl]$ is more labile than in $[(\pi\text{-}C_5H_5)Rh(C_2H_4)_2]$, even though ethylene exchange is not observed on the NMR time scale in either case.

The reaction of Ph_3P with III and IV caused displacement of MeLL in both cases, the free ligand being identified by ^1H NMR spectroscopy. Products from III were not obtained pure, but IV yielded $[Rh(cod)(Ph_3P)Cl]$, with a ^1H NMR spectrum identical with literature data [52]. The comparable reaction of $[Rh(bipy)(cod)]^+$ with Ph_3P gives the five-coordinate cation $[Rh(bipy)(cod)(Ph_3P)]^+$ [44]. Hence it appears that the analogous $[(MeLL)Rh(cod)(Ph_3P)]^+$ cation is less stable, at least in the presence of chloride ion. A strong affinity of chloride ion for Rh^I species has been noted [53].

Complexes III and IV were studied as possible hydrogenation catalyst precursors, in reactions involving molecular hydrogen and monoolefins or α,β-unsaturated carbonyl compounds. Initial results indicate that III will catalyse the hydrogenation of terminal and internal olefins, but not crotonaldehyde or mesityl oxide, under neutral conditions in methanol. The catalytic hydrogenations showed relatively long induction periods, as has been observed for other $[Rh(N\text{-}N)(diolefin)]^+$ systems [39]. The low reactivity of Rh^I systems containing cod or nbd as the diolefin [39,41], and the need for "pre-hydrogenation" of the catalyst solution to prevent the formation of inactive species, have been described. The greater effectiveness of $[Rh(N\text{-}N)(diolefin)]^+$ catalyst precursors under alkaline conditions, and specificity for carbonyl group hydrogenation, have also been reported [38].

Experimental

All reagents were handled under dry nitrogen using Schlenk equipment and a Vacuum Atmospheres Model HE493 drybox. Solvents were dried and distilled under nitrogen. Research chemicals were purchased from commercial suppliers. The ligand $PhCH(H_2pz)_2(LL)$ [54] and the complexes $[Rh(C_2H_4)_2Cl]_2$ [10] and $[Rh(cod)Cl]_2$ [11] were prepared according to published procedures. C, H, N elemental analyses were performed by the University Analyst, Simon Fraser University. Molecular weights were measured using a Hitachi-Perkin-Elmer Model 115 osmometer, and conductivities were determined using a conventional conductivity cell coupled with a Leeds and Northrup potentiometer 7645, a General Radio Co. 1433-H decade resistor, a Tetronix Inc. Type 503 oscilloscope detector and Hewlett Packard Model 200AB audio oscillator. The other instruments utilized were the Perkin-Elmer 457 infrared spectrometer, the Hewlett Packard 5985 mass spectrometer, and the Varian A56/60, EM360 and XL100 nuclear magnetic resonance spectrometers, the latter having Fourier transform and nuclear decoupling facilities.

Preparation of $PhCH(Me_2pz)_2(MeLL)$

A mixture of 1,1′-carbonylbis(3,5-dimethylpyrazole) (9.2 mmol), anhydrous cobalt(II) chloride (~4 mg) and 5 ml of benzaldehyde was heated at 90—95°C for 16 hours in a reaction tube fitted with a Rotaflow valve. At intervals the tube was cooled and liberated CO_2 was removed under vacuum. The mixture was filtered, the excess benzaldehyde was distilled off under vacuum, and the product $PhCH(Me_2pz)_2$ was distilled under high vacuum.

Preparations of complexes

The following complexes were prepared as described, on a 1 millimolar scale.

$[(LL)Rh(C_2H_4)Cl]$ (I). A mixture of $[Rh(C_2H_4)_2Cl]_2$ and LL in benzene was stirred at room temperature for 20 hours. The product, which was precipitated as a yellowish powder, was filtered off and washed with hexane.

$[(LL)(Rh(cod)Cl)_2]$ (II). A mixture of $[Rh(cod)Cl]_2$ and LL in 50/50 benzene/hexane (1 : 1 molar ratio) was stirred at room temperature for 6 hours. The product, which was precipitated as a yellow solid, was filtered and washed with hexane.

$[(MeLL)Rh(C_2H_4)_2Cl]$ (III). A mixture of MeLL and $[Rh(C_2H_4)_2Cl]_2$ in benzene (2 : 1 molar ratio) was stirred at room temperature for 3 hours. The solution was evaporated to dryness under vacuum, and the orange product was recrystallized from benzene/hexane.

$[(MeLL)Rh(cod)]Cl$ (IV). A mixture of MeLL and $[Rh(cod)Cl]_2$ in benzene/hexane (2 : 1 molar ratio) was stirred at room temperature for 6 hours. The product separated as a yellow solid. It was filtered off and washed with hexanes.

Complex IV was also obtained when a mixture of $[(MeLL)Rh(C_2H_4)_2Cl]$ (II) and cyclooctadiene (1 : 1 molar ratio) in benzene was stirred at room temperature for 20 hours.

$[(MeLL)Rh(cod)]BPh_4$ (V). Approximately equimolar methanolic solutions of $NaBPh_4$ and $[(MeLL)Rh(cod)]Cl$ were mixed. Within a few minutes, the product separated as a pale yellow solid. It was recrystallized from CH_2Cl_2/heptane.

The reaction of $[(MeLL)Rh(cod)]Cl$ (IV) with hydrogen chloride

A solution of $[(MeLL)Rh(cod)]Cl$ (0.237 mmol) in methanol (20 ml) was frozen in liquid N_2 and degassed. Anhydrous HCl (0.237 mmol) was transferred to the reaction vessel, which was allowed to warm to room temperature. A yellow precipitate quickly formed. The mixture was stirred for 2 hours, and the precipitate was filtered off and washed with methanol. The ^1H NMR spectrum of this product was identical with that of $[Rh(cod)Cl]_2$. Yield, 75%. The filtrate was pumped dry, leaving an off-white residue identified as $Me_2pzH \cdot HCl$. Independent studies showed that the ligand MeLL is cleaved by HCl in methanol and in toluene [47].

The reaction of $[(MeLL)Rh(cod)]Cl$ (IV) with carbon monoxide

Carbon monoxide was passed into a solution (yellow) of $[(MeLL)Rh(cod)]Cl$ (0.525 mmol) in methanol at room temperature. The colour of the solution quickly faded, and a pale yellow compound was precipitated. The product,

$[(\text{MeLL})\text{Rh}(\text{CO})_2]^+[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$ (VI) was collected, washed with methanol, and pumped dry. M. pt. 137—138°C (dec.). Yield, 50%. IR spectrum (KBr disc, ν(CO) region, 2100s, 2066s, 2042s, 1988w, 1982s, 1960(sh) cm^{-1}). Bands attributable to MeLL were also present. ^{1}H NMR spectrum, τ values, 1.81 (s, 1 H, methylidene CH), 2.42—2.54 and 3.20—3.37 (phenyl multiplets), 3.66 (b, 2 H, 4-H), 7.39(s) and 7.59(s) (6 H, 3-CH_3 and 5-CH_3).

Complex VI was also obtained when solutions of IV or III in diethyl ether were treated with carbon monoxide.

The reaction of $[(\text{MeLL})\text{Rh}(\text{CO})_2]^+[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$ (VI) with NaBPh_4

Approximately equimolar solutions of VI and NaBPh_4 in aqueous methanol were mixed. A brown precipitate was obtained. The IR spectrum of the product (KBr disc) showed ν(CO) bands at 2100s and 2040s cm^{-1}, and absorptions due to coordinated MeLL. The product is formulated as $[(\text{MeLL})\text{Rh}(\text{CO})_2]\text{BPh}_4$ (VII).

The reaction of [(MeLL)Rh(cod)]Cl (IV) with Ph_3P

A mixture of [(MeLL)Rh(cod)]Cl (0.33 mmol) and Ph_3P (0.37 mmol) in methanol (25 ml) was stirred at room temperature under nitrogen. The solution slowly became orange over a period of ~2 hours, and a yellow precipitate gradually appeared. After 18 hours, the product $[\text{Rh}(\text{cod})(\text{Ph}_3\text{P})\text{Cl}]$ (VIII) was filtered off and washed with methanol. The filtrate was evaporated to dryness under vacuum, giving a residue which was separated by washing with hexanes into a further crop of VIII (insoluble in C_6H_{12}) and MeLL (soluble in hexanes; identified by its ^{1}H NMR spectrum). Overall yield of VIII, 40%. The ^{1}H NMR spectrum of VIII was identical with the spectrum reported for $[\text{Rh}(\text{cod})(\text{Ph}_3\text{P})\text{Cl}]$ [52], and with that of a sample of this compound prepared in our labs.

The above reaction was repeated, using toluene in place of methanol as solvent. The products of reaction were soluble in toluene. After 24 hours, the solvent was pumped off, leaving a pale yellow residue. Extraction with hexanes gave an insoluble component, identified as $[\text{Rh}(\text{cod})(\text{Ph}_3\text{P})\text{Cl}]$, and a soluble component, identified as MeLL.

Studies of $[(\text{MeLL})\text{Rh}(\text{C}_2\text{H}_4)\text{Cl}]$ (III) and [(MeLL)Rh(cod)]Cl (IV) as hydrogenation catalysts

The apparatus consisted of a reaction vessel fitted with a rubber septum cap and connected via a side-arm to a hydrogen bulb and an oil manometer. The oil was pre-saturated with hydrogen at 760 Torr, and solutions of the reagents were added by syringe via the septum cap. The reaction vessel was protected from light by an aluminum foil covering, and the reaction mixture was stirred magnetically.

In a typical experiment, 0.5 ml of *trans*-3-hexene and 1.0 ml of a methanolic solution (5.68×10^{-2} *M*) of III were transferred successively to the reaction vessel. The stirrer was immediately switched on. An increase in pressure was observed for several minutes, followed by an induction period of about 30 minutes. Thereafter the slow decrease in pressure was monitored for several hours.

A metallic precipitate appeared when the reaction was essentially complete. The hydrocarbon product of hydrogenation was separated by fractionation under vacuum, and identified as n-hexane by ^{1}H NMR and coupled GC/mass spectroscopy.

The experiment was repeated, using methanol-d_4 as solvent. The mass spectrum of the product showed no evidence of deuterated hexanes.

Similar experiments using 1-hexene, *trans*-2-hexene, cyclohexene, 1,5-hexadiene, and *trans*-2-pentene were carried out. In each case the corresponding saturated hydrocarbon was produced. With crotonaldehyde and mesityl oxide, no hydrogen uptake was observed.

The use of solvents other than methanol was investigated. The catalyst, complex III, was insufficiently soluble in benzene, and unstable in THF in the presence of hydrogen. Nitrobenzene was slowly reduced by H_2 in the presence of III.

The use of [(MeLL)Rh(cod)]Cl (IV) in place of III as a catalyst for the hydrogenation of *trans*-3-hexene was studied. No hydrogen uptake was observed.

Acknowledgment

The financial support of the Natural Sciences and Engineering Research Council of Canada is acknowledged.

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