SYNTHESIS OF PYRAZOLIDE-BRIDGED HETEROMETALLIC BINUCLEAR COMPLEXES

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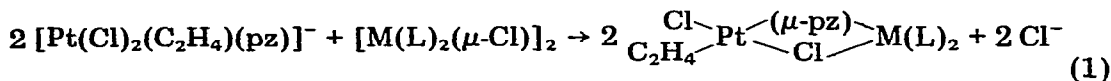
Summary

A convenient synthetic procedure is described for the synthesis of heteronuclear bimetallic complexes involving platinum and one other Group VIII metal with a single bridging pyrazolide group. The reagent used is the nucleophilic anion, *trans*-$[Pt(Cl_2)(pz)(C_2H_4)]^-$, ($pz = C_3H_3N_2^-$) generated in situ by deprotonation of the Zeise's adduct of pyrazole which will react with reasonably labile substrates to yield binuclear products. Spectroscopic and chemical properties of the products are discussed.

Introduction

Dinuclear transition metal complexes have received much attention due to their importance in the study of electron transfer reactions [1] and homogeneous catalysis [2]. Synthetic pathways to the formation of these complexes which allow systematic synthesis of a series of related binuclear species are of interest. We wish to report a direct method of synthesis for dinuclear complexes containing a single pyrazolato bridging ligand, utilizing a Pt^{II} olefin complex, which allows considerable latitude to vary the second metal center and the coordination spheres about the metals. The synthetic reaction for heteronuclear bimetallic complexes can be written:

$$2\ [Pt(Cl)_2(C_2H_4)(pz)]^- + [M(L)_2(\mu\text{-}Cl)]_2 \rightarrow 2\ \underset{C_2H_4}{\overset{Cl}{\diagdown}}Pt\overset{(\mu\text{-}pz)}{\underset{Cl}{\diagup\diagdown}}M(L)_2 + 2\ Cl^- \quad (1)$$

Results and discussion

Recently, we have observed that deprotonation of N(2) of the pyrazole ring of the complex *trans*-$[Pt(Cl)_2(pzH)(C_2H_4)]$ (1) (where pzH is pyrazole, $C_3N_2H_4$) yields a nucleophilic species which will displace sufficiently labile ligands on other class B metal complexes. For example, the diplatinum complex $[(C_2H_4)$-

SCHEME 1

$[COD] = \eta^4 - 1{,}5 - \text{cyclooctadiene}$
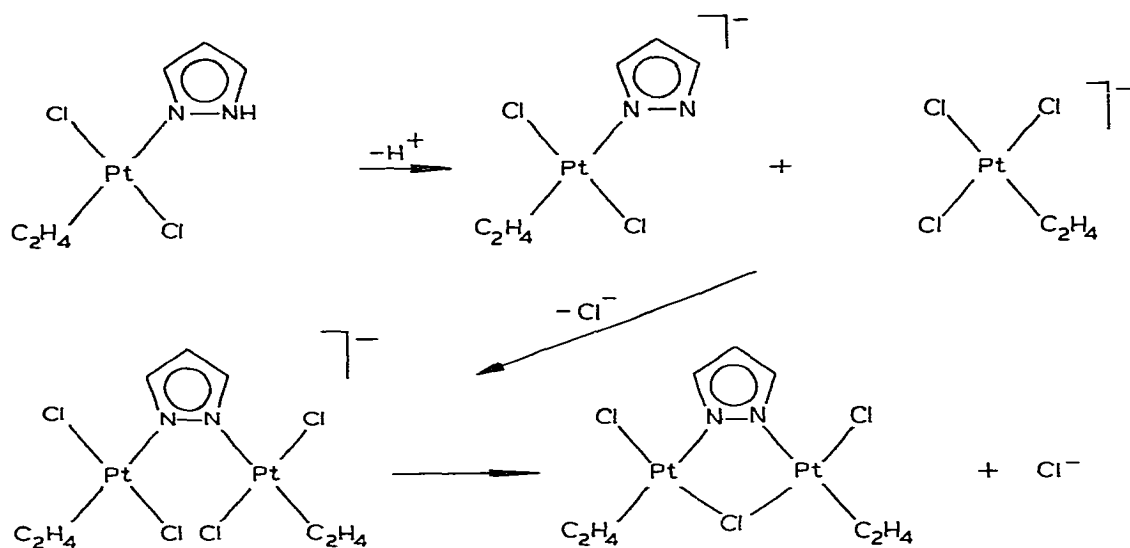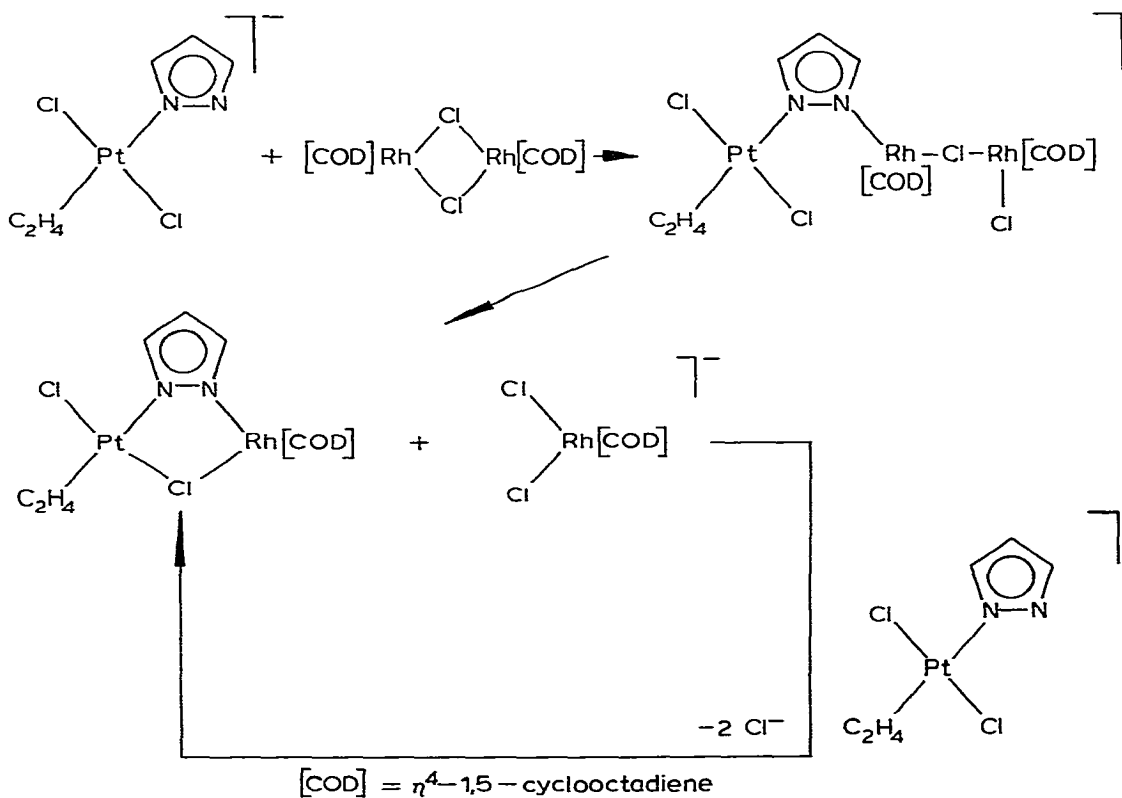
SCHEME 2

(Cl)Pt(μ-Cl)(μ-pz)Pt(Cl)(C$_2$H$_4$)] (**2**) is obtained when the mononuclear anionic pyrazolato complex reacts with an equivalent of the anion of Zeise's salt [3] (see Scheme 1). It is well known that dimeric complexes, of the type [L$_2$MCl]$_2$, are readily cleaved by donor ligands to yield two mononuclear square planar species [4]. This suggested a pathway to dinuclear anionic complexes, similar to the one in Scheme 1, leading to the formation of neutral complexes containing two different metal centers (see Scheme 2). This reaction scheme (see eq. 1) has been used successfully for cases where M is Pd^{II}, or Rh^{I} and L is η^3-allyl, η^3-methallyl or 1,5-cyclooctadiene with pyrazolide or 3,5-dimethylpyrazolide as the bridging ligand.

Stoichiometric mixtures of *trans*-[Pt(Cl)$_2$(pzH)(C$_2$H$_4$)] and [L$_2$MCl]$_2$ substrates in CDCl$_3$ show no evidence for reaction in the absence of base. Reaction can be initiated by the addition of a non-coordinating base such as triethylamine and the course of the reaction followed by NMR. A convenient synthetic path involves the use of Na$_2$CO$_3$(s) to supply the base equivalents. Stirring the reactants in chloroform with an excess of powdered Na$_2$CO$_3$ for 3—4 hours was usually sufficient for complete reaction. Filtration to remove the insoluble salts and evaporation of the solvent leads to an essentially quantitative yield of the desired product in most cases. These materials are air-stable in the solid; however, partial decomposition was noted in chloroform solution over a period of days for some samples, particularly those involving methyl-substituted pyrazoles. Kinetically inert substrates cannot be used in this synthesis due to a side reaction to produce **2**:

$$[Pt(Cl)_2(C_2H_4)(pz)]^- + Pt(Cl)_2(C_2H_4)(Hpz) \rightarrow 2 + Hpz + Cl^- \qquad (2)$$
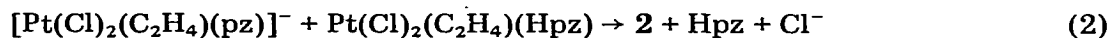
For example, attempts to produce trinuclear species by the reaction of **2** with [Pt(Cl)$_2$(C$_2$H$_4$)(pz)]$^-$ fail for this reason.

The proton and ^{13}C magnetic resonance spectra of the binuclear products are consistent with the assigned structure and could be used to characterize the binuclear species, such as [(C$_2$H$_4$)(Cl)Pt(μ-Cl)(μ-3,5-Me$_2$pz)Pd(Meallyl)], which could only be generated in situ. One characteristic spectral change noted for all the binuclear complexes is a decrease in the $J(^{195}$Pt—^{1}H) coupling to the olefin ligand of the platinum center from 62 Hz in *trans*-[Pt(Cl)$_2$(pzH)(C$_2$H$_4$)] to 54—58 Hz in the binuclear products. We suggest that the change in ^{195}Pt—olefin coupling is a consequence of an increase in σ-bonding by the pyrazolide group compared to the neutral pyrazole ligand of the mononuclear complex, *trans*-Pt(C$_2$H$_4$)Cl$_2$(pzH). An increase in the Pt(6s) contribution in the Pt—pz bond would lead to a corresponding decrease in the contribution of this orbital to the Pt—olefin σ bond. Braterman [12] has noted that a correlation is expected between ^{195}Pt—H coupling and Pt(6s) character in Pt—olefin bonds. A comparable trend is observed in the ^{195}Pt—^{13}C coupling constants (see Table 2). Similar correlations between ^{195}Pt—^{13}C coupling constants and olefin-to-platinum σ bonding have been reported [14]. The upfield shift in the δ(^{1}H) for the olefin ligand may indicate increased Pt-to-C$_2$H$_4$ π-bonding similar to variation of δ(C$_2$H$_4$) observed in *trans*-Pt(C$_2$H$_4$)Cl$_2$(z-pyo) (where z-pyo are 4-substituted pyridine-*N*-oxides) [17]. No similar molecular interpretation exists for δ(^{13}C) for reasons noted in the literature [18]. The chemical shifts and coupling constants for the various complexes are collected in Tables 1 and 2. The PMR

TABLE 1

60 MHz PROTON NMR DATA [a]

	Olefin		Azaromatic						Other (δ)
	δ	J(195Pt)	δ(H(5)) [c]	J(195Pt)	δ(H(3)) [c]	J(195Pt)	δ(H(4)) [c]	J(195Pt)	
trans-Pt(Cl)$_2$(pzH)(C$_2$H$_4$) [b]	4.77(s)	62	8.51(m)	—	7.79(m)	—	5.96(m)	—	(11.90(s), N(2)-H)
trans-Pt(Cl)$_2$(3,5-Me$_2$pzH)(C$_2$H$_4$)	4.87(s)	61.3	—	—	—	—	6.01(s)	—	(10.78(s), N(2)-H); (2.57(s), 5-Me); (2.27(s), 3-Me)
[(C$_2$H$_4$)ClPt(μ-Cl)(μ-pz)PtCl(C$_2$H$_4$)] [b]	4.62(s)	54	8.24(d)	11.7	8.24(d)	11.7	6.34(m)	—	
[(C$_2$H$_4$)ClPt(μ-Cl)(μ-3,5-Me$_2$pz)PtCl(C$_2$H$_4$)]	4.54(s)	58	—	—	—	—	5.93(s)	15.5	(2.57(s), 3,5-Me)
[(C$_2$H$_4$)ClPt(μ-Cl)(μ-pz)RhCOD]	4.51(s)	56.1	8.09(s)	13.7	6.99(s)	11.6	6.17(t)	8.3	(4.26(s), 2.17(m), COD)
[(C$_2$H$_4$)ClPt(μ-Cl)(μ-pz)Pd(η^3-allyl)]	4.52(s)	54.8	8.18(d)	12.4	7.49(d)	10.3	6.21(t)	8.3	(5.52(m); C(2)-H; (4.04(d), Hs); (3.11(d), Ha)
[(C$_2$H$_4$)ClPt(μ-Cl)(μ-pz)Pd(η^3-methylallyl)]	4.59(s)	56.5	8.25(d)	11.8	7.56(d)	10.5	6.25(t)	8.3	(3.82(d), Hs); (2.99(d)Ha); (2.15(s); C(2)-Me)
[(C$_2$H$_4$)ClPt(μ-Cl)(μ-3,5-Me$_2$pz)Pd(η^3-allyl)]	4.68(s)	56.0	—	—	—	—	5.91(s)	11.8	(5.62(m), C(2)-H); (4.26(d), Hs); (2.98(d), Ha); (2.50(s), 5-Me); (2.24(s), 3-Me)

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| $[(C_2H_4)ClPt(\mu\text{-}Cl)(\mu\text{-}3,5\text{-}Me_2pz)Pd(\eta^3\text{-}methallyl)]$ | 4.71(s) | 56.5 | — | — | — | 5.94(s) | 12.0 | — | (4.02(s), Hs); (3.02(s), Ha); (2.48(s), 5-Me); (2.23(s), 3-Me); (2.23(s), C(2)-Me) |

[a] All δ values are in ppm relative to TMS; Solvent = $CDCl_3$; $J(^{195}Pt) = J(^{195}Pt\text{–}^1H)$ coupling const. in Hz; s, d, t, m = singlet, doublet, triplet and broad multiplet respectively; due to proton–proton coupling; N(2)-H = pzH N(2) proton; 5-Me = methyl substituted on ring atom 5; Hs, Ha, C(2)-H = *syn*, *anti* and central proton on allyl anion. [b] Differences between these and earlier values (ref. 3a) due to an instrumental problem in sweep width calibration. [c] The numbering scheme used here differs from that for isolated pyrazole rings. We have chosen to number the ligating nitrogen of the neutral pyrazole as N(1) and the second nitrogen as N(2). For heterobimetallic complexes the nitrogen bonded to platinum is designated N(1).

TABLE 2

22.5 MHz ^{13}C NMR DATA [a]

	Olefin		Azoaromatic						Other (δ)
	δ	$J(^{195}Pt)$	$\delta(C(5))$	$J(^{195}Pt)$	$\delta(C(3))$	$J(^{195}Pt)$	$\delta(C(4))$	$J(^{195}Pt)$	
trans-[Pt(C₂H₄)Cl₂(pzH)]	72.2	180	139.5	48	130.3	30	106.8	34	—
[(C₂H₄)ClPt(μ-Cl)(μ-pz)PtCl·(C₂H₄)]	74.0	156	141.4	61 [b]	141.4	37 [b]	104.0	35	—
[(C₂H₄)ClPt(μ-Cl)(μ-pz)·Pd(η³-C₃H₅)]	72.8	157	139.2	64	142.8	44	104.4	34	(61.9, C(t)); (113.3, C(c))
[(C₂H₄)ClPt(μ-Cl)(μ-pz)·Rh(COD)]	73.0	156	139.9	60	138.5	43	104.2	35	(82.7, C(N); J(¹⁰³Rh) 10); (79.2, C(Cl); J(¹⁰³Rh) = 15); (30.8, CH₂)

[a] All δ values are in ppm downfield from TMS; Solvent = $CDCl_3$; $J(^{195}Pt) = {}^{195}Pt\text{–}^{13}C$ coupling constant in Hz; C(t) = terminal carbon atoms of $\eta^3\text{-}C_3H_5$; C(c) = central carbon of $\eta^3\text{-}C_3H_5$; C(N) = COD olefinic carbons *trans* to N; C(Cl) = COD olefinic carbons *trans* to Cl; CH₂ = COD aliphatic carbons; $J(^{103}Rh) = {}^{103}Rh\text{–}^{13}C$ coupling constant in Hz. [b] The C(5), C(3) carbon atoms are chemically equivalent. The two $J(^{195}Pt)$ represent two-bond (61 Hz) and three-bond coupling constants.
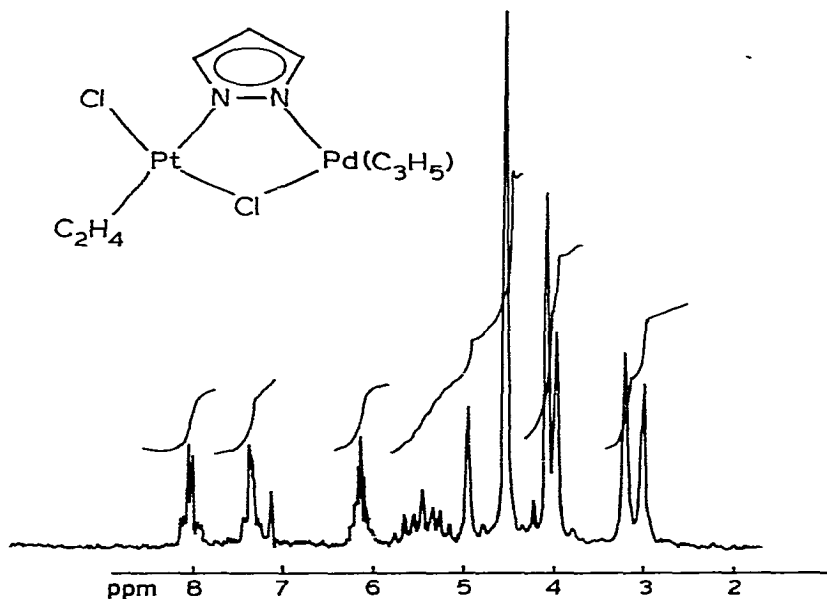
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Fig. 1. Proton magnetic resonance spectrum of [(C$_2$H$_4$)(Cl)Pt(μ-Cl)(μ-pz)Pd(C$_3$H$_5$)] at 60 MHz ($T \sim 40°$C).

resonance spectrum of [(C$_2$H$_4$)(Cl)Pt(μ-Cl)(μ-pz)Pd(η^3-allyl)] reproduced in Fig. 1 is typical of the binuclear species showing an upfield shift of the olefin resonance (compared to 1) and decrease in J(^{195}Pt—^{1}H) characteristic of the binuclear complexes. The PMR spectra for these complexes suggest that a variety of types of fluxional behavior occur at rates which are fast relative to the PMR time scale at ambient probe temperature. At low temperatures ($T \sim$ —40°C), the olefin resonance of 2 shows signs of restricted rotation [7], which is typical of platinum(II)-olefin complexes. For the allyl complexes, the observation of a doublet for the *syn* protons and a second doublet for the *anti* protons (due to coupling to the C(2) proton) suggests that allyl rotation is rapid and $\eta^3 \rightarrow \eta^1$ rearrangement slow at the probe temperature [8]. Alternatives to allyl rotation involving exchange or a twisting mechanism are possible [8,9]. Detailed studies of the fluxional behavior of these complexes are underway.

Infrared spectral measurements support the assignment of a binuclear structure to these complexes. First, the absence of bands at 3300 cm^{-1} associated

TABLE 3

ν(C=C) AND ν(Pt—L) FOR SELECTED PYRAZOLE AND PYRAZOLIDE OLEFIN COMPLEXES

	ν(C=C) [b]	ν_a(Pt—C)	ν_s(Pt—C)	ν(Pt—Cl)	ν(Pt—N)
trans-Pt(C$_2$H$_4$)Cl$_2$pzH	1513, 1245	485	390	338	225
(C$_2$H$_4$)ClPt(μ-Cl)(μ-pz)PtCl(C$_2$H$_4$)	1520, 1255	472	378	349	(322?)
(C$_2$H$_4$)ClPt(μ-Cl)(μ-pz)Pd(η^3-C$_3$H$_5$)	1490, 1242	498	385	340	—
(C$_2$H$_4$)ClPt(μ-Cl)(μ-pz)Rh(COD)	[a] 1250	477	380	330	—

[a] Obscured by COD ν(C=C). [b] Coupled ν(C=C), ν_s(CH$_2$) vibrations.

with ν(NH) and absorptions at ca. 720 and 580 cm^{-1} assigned by Reedijk [13] to out-of-plane N—H bending are consistent with deprotonation of the aromatic ligand. Second, the less complex spectrum of the binuclear species is consistent with an effective symmetry of "C_{2v}" for the bridging pyrazolide ligand [10]. A partial list of infrared frequencies is given in Table 3. These observed values are consistent with previous observations [15]. Based upon the method of Powell, a reduction in the olefin double-bond character of approximately 12—15% occurs in each of these complexes [16].

Due to the abundance of dimeric complexes containing two symmetrical chloride bridges, many mixed metal dinuclear complexes of the type described are potentially available. The fact that the platinum-pyrazole starting material and many of the dimeric substrates are air stable enables this synthetic process to be performed without the necessity of a controlled atmosphere. The remaining olefin moiety of the platinum(II) retains the characteristic chemical reactivity of a coordinated olefin [11]. For example, olefin exchange, ethylene displacement by CO, and nucleophilic attack upon the olefin (by excess pyrazole) were observed.

Preliminary investigation of the catalytic activity of the diplatinum complex in olefin hydrogenation was carried out using cyclohexene. One ml of a saturated solution of the complex (ca. 10^{-2} M prepared under N_2) was injected into the pear-shaped flask of a constant pressure batch reactor which had been flushed with H_2 gas (1 atmosphere) at 30°C. Hydrogenation of cyclohexene to cyclohexane was indicated by uptake of H_2, gas chromatography and NMR spectra of reaction mixtures. Approximately 13% of the cyclohexene has hydrogenated in the first five minutes. No decomposition of the complex was detected. Infrared spectra of aliquots evaporated before and after introduction of hydrogen are identical and presumably correspond to a cyclohexene binuclear complex. Further investigation of the catalytic activity of the binuclear complexes is in progress.

Experimental

Pyrazole, [(COD)RhCl]$_2$, Na$_2$CO$_3$ and all solvents were purchased commercially and used without further purification. Zeise's salt [5] and [(η^3-CH$_2$CR'-CH$_2$)PdCl]$_2$ (where R' = H and CH$_3$) were prepared by standard synthetic procedures [6]. The syntheses of trans-[Pt(Cl)$_2$(pzH)(C$_2$H$_4$)] and trans-[Pt(Cl)$_2$-(3,5-MepzH)(C$_2$H$_4$)] were performed as previously reported [3]. The PMR measurements were performed on Varian EM 360 or Varian A-60 NMR spectrometers. The ^{13}C NMR spectra were obtained in CDCl$_3$(TMS) using a JEOL FX90Q spectrometer at 22.5 MHz. Infrared spectra were obtained using a Perkin-Elmer 283 IR spectrophotometer. Melting point ranges were measured on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Guelph Chemical Laboratories Ltd., Guelph, Canada.

[(Cl)(C$_2$H$_4$)Pt(μ-Cl)(μ-R$_2$pz)Pt(Cl)(C$_2$H$_4$)], (R = H, CH$_3$)

These complexes were prepared by the following modification of the published procedure [3]. A reaction mixture was prepared by adding 0.200 g of

trans-[Pt(C')$_2$(Hpz)(C$_2$H$_4$)] (0.55 mmol) and 0.187 g K[PtCl$_3$(C$_2$H$_4$)] (0.55 mmol) to 5.0 ml of CHCl$_3$ (or CDCl$_3$). Excess powdered Na$_2$CO$_3$ (0.5 g) was added and the reaction stirred for 12 hours at 25°C. After filtration to remove insoluble salts, evaporation of the solvent gave essentially quantitative yield of the desired product. (m.p. = 125—135°C, dec. to a red-brown product). Analysis (R = H): Found: C, 13.53; N, 4.55; H, 2.00. C$_7$H$_{11}$Cl$_3$N$_2$Pt$_2$ Calcd.: C, 13.57; N, 4.52; H, 1.79%.

[(C$_2$H$_4$)ClPt(μ-Cl)(μ-pz)Rh(1,5-COD)]

A chloroform solution was prepared by the addition of 0.20 gm of [(COD)-RhCl]$_2$ (0.4 mmol) and 0.29 gm of *trans*-[Pt(Cl)$_2$(pzH)(C$_2$H$_4$)] (0.8 mmol) to a minimum amount of solvent (5—10 ml). An excess of powdered Na$_2$CO$_3$ (0.5 g) was introduced and the reaction mixture stirred for 2—4 h. The insoluble salts were removed by filtration through a glass sintered filter. The yellow-orange filtrate yielded [(Cl)(C$_2$H$_4$)Pt(μ-Cl)(μ-pz)Rh(COD)] upon slow evaporation of the solvent. (Melting point 222—224°C; Analysis. Found: C, 27.57; N, 4.25; H, 3.38. C$_{13}$H$_{19}$Cl$_2$N$_2$PtRh Calcd.: C, 27.29; N, 4.89; H, 3.32%. See Tables 1 and 2 for spectral data.)

[Cl(C$_2$H$_4$)Pt(μ-Cl)(μ-pz)Pd(η^3-CH$_2$CHCH$_2$)]

A reaction solution was prepared by the addition of 0.20 g [(allyl)-PdCl]$_2$ and 0.40 g (2 equivalents) *trans*-[Pt(Cl)$_2$pzH(C$_2$H$_4$)] to 5—10 ml CHCl$_3$. This solution was introduced and was stirred for 2—4 h with an excess of Na$_2$CO$_3$. The insoluble salts were removed by filtration through a glass sintered filter and the product isolated by evaporation of the solvent. (Melting point 139—141°C; Analysis. Found: C, 19.13; N, 5.52; H, 2.47. C$_8$H$_{12}$Cl$_2$N$_2$PdPt Calcd.: C, 18.91; N, 5.51; H, 2.38%. See Tables 1 and 2 for spectral data.)

Additional complexes

Complexes involving 3,5-dimethylpyrazolide bridge to Pd^{II}-allyl moieties could not be isolated as crystalline solids; however, these materials could be generated in situ for PMR measurements by the procedure outlined above. Evaporation of solution of these materials gave oils which decomposed on standing in air. The PMR spectra are consistent with formation of the proposed binuclear complexes.

Acknowledgements

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