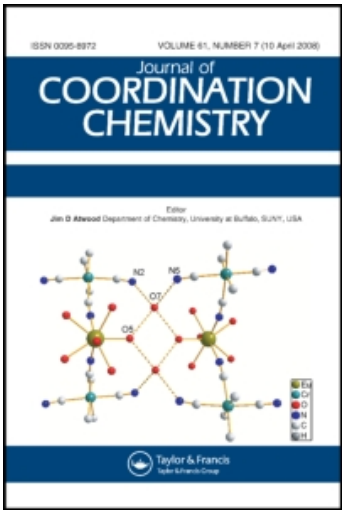

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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Frederick Pesa[a]; Len Spaulding[a]; Milton Orchin[a]
[a] Department of Chemistry, University of Cincinnati, Cincinnati, Ohio, U.S.A.

To cite this Article Pesa, Frederick , Spaulding, Len and Orchin, Milton(1975) 'LIGAND EXCHANGE AND LIGAND TRADING IN *TRANS*-[PtX_2(OLEFIN) (PYRIDINE)] COMPLEXES', Journal of Coordination Chemistry, 4: 4, 225 — 230
To link to this Article: DOI: 10.1080/00958977508075904
URL: http://dx.doi.org/10.1080/00958977508075904

J. Coord. Chem.
1975, Vol. 4, pp. 225–230

LIGAND EXCHANGE AND LIGAND TRADING IN *TRANS*-[PtX_2(OLEFIN) (PYRIDINE)] COMPLEXES

FREDERICK PESA, LEN SPAULDING and MILTON ORCHIN†

Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221, U.S.A.

(*Received December 3, 1974*)

The ^{1}H nmr spectra of freshly prepared $CDCl_3$ solutions of the complexes *trans*-[$PtCl_2$(olefin)(L)], where L is pyridine or a substituted pyridine, show no coupling between ^{195}Pt and the α protons of pyridine ($^3J_{Pt-NCH}$) owing to rapid exchange of complexed L with free L. On standing, the adventitious free L is gradually consumed by formation of *trans*-[$PtCl_2(L)_2$] and the spectra of the aged solutions show the coupling. When $CDCl_3$ solutions of [$PtBr_2(Ol_b)(L_b)$] and [$PtCl_2(Ol_a)(L_a)$], where $Ol_a = C_2H_4$, are mixed, a total of 6 ethylene complexes can be identified in solution. Accordingly halogen trading, Ol trading or/and L trading occurs and the solution probably contains a total of 12 complexes.

INTRODUCTION

The standard procedure for preparing the titled complexes consists of treating Zeise's salt (or its analogs) with a stoichiometric quantity of the desired pyridine (or related base) in water:

$$K[PtCl_3(olefin)] + L \longrightarrow \underset{\mathbf{1}}{trans\text{-}[PtCl_2(olefin)(L)]} + KCl \quad (1)$$

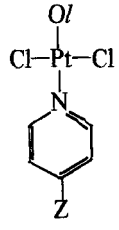
We have recently reported[1,2] that the ^{1}H nmr spectrum of *trans*-[$PtCl_2(C_2H_4)$(isoquinoline)] **1***a*, taken immediately after dissolving it in $CDCl_3$ exhibits no $^3J_{Pt-NCH}$ because of rapid exchange of complexed isoquinoline with adventitious free isoquinoline. The free base is apparently trapped in **1***a* during its precipitation. However, after standing for several days, the ^{1}H nmr spectrum of the aged $CDCl_3$ solution shows $^3J_{Pt-NCH}$ owing to the consumption of free ligand by the formation of *trans*-[$PtCl_2$(isoquinoline)$_2$]:

$$L + trans\text{-}[PtCl_2(C_2H_4)L)] \longrightarrow trans\text{-}[PtCl_2(L)_2] + C_2H_4 \quad (2)$$

When adventitious free isoquinoline is removed either by treatment with a cation exchange resin or by extraction from the fresh solution of **1***a* with aqueous HBF_4, the spectrum of **1***a* shows $^3J_{Pt-NCH}$.

In an earlier paper[3] we summarized the ^{1}H nmr spectra of the related complexes, **2***a*–**2***k*.

An analysis of the temperature-dependent ^{1}H nmr spectra of these complexes showed a good correlation between the temperature required to observe coupling of the α protons of pyridine and the nature of Z. At that time we did not suspect that the ^{1}H nmr spectra of the complexes in $CDCl_3$ at room temperature might change on long standing. We now report that this is indeed the case.



2

	Z	Ol
(*a*)	H	C_2H_4
(*b*)	CH_3	C_2H_4
(*c*)	OCH_3	C_2H_4
(*d*)	CO_2CH_3	C_2H_4
(*e*)	CN	C_2H_4
(*f*)	CH_2OH	C_2H_4
(*g*)	CO_2CH_3	*cis*-C_4H_8
(*h*)	CO_2CH_3	*t*-C_4H_8
(*i*)	CH_3	*cis*-C_4H_8
(*j*)	CN	*cis*-C_4H_8
(*k*)	H	*cis*-C_4H_8

We have also reported previously[3] that when $CDCl^3$ solutions of two similar complexes are mixed, two new complexes are formed, making a total of four complexes in solution:

$$[PtCl_2(Ol_a)(L_a)] + [PtCl_2(Ol_b)(L_b)] \rightleftharpoons [PtCl_2(Ol_a)(L_b)] + [PtCl_2(Ol_b)(L_a)] \quad (3)$$

(We will hereafter refer to reactions such as (3), which involve exchange of similar ligands, as ligand trading.) On discovering[1] that small quantities of L_a and L_b are trapped in their respective complexes during their preparation, the possibility that free ligand might have initiated trading reaction (3), needed to be examined. We have accordingly reinves-

†Author to whom correspondence should be addressed.

tigated such trading reactions but in considerably more detail.

RESULTS AND DISCUSSION

1. Ligand Exchange

Our previous ^{1}H nmr data for complexes **2** were obtained on fresh $CDCl_3$ solutions and hence these reported data all showed the absence of $^3J_{Pt-NCH}$. We now find that if the $CDCl_3$ solutions of compounds **2***a*–**2***i* are allowed to stand 5–10 days at room temperature, the ^{1}H nmr spectra of all aged solutions but **2***e* show coupling of the α protons. The complex **2***e* showed no coupling even after 3 months of standing at room temperature in $CDCl_3$ solution. Attempted extraction with aqueous HBF_4 of any free ligand (if present) in this complex resulted in a reaction instead, and the formation of a different complex which has yet to be characterized.

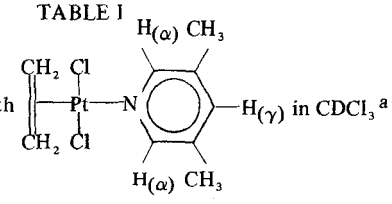
The time required for solutions of complexes **2** to show coupling was erratic and did not correlate well with either the nature of Z or Ol probably because the quantity of adventitious free ligand in the complexes varied somewhat.

The ^{1}H nmr spectra of complexes **2** which showed coupling after long standing at room temperature were essentially identical with the corresponding spectra taken of freshly dissolved complexes (containing adventitious free ligand) at the low temperatures required for coupling to appear. Representative data are shown in Table I. Since there is a possibility of reaction of the complexes with TMS, an external TMS lock was used for the low temperature spectra, and an internal cyclohexane lock was used for the room temperature spectra. The internal standard was $CHCl_3$.

The behavior of the pyridine complexes described above is consistent with the behavior of *trans*-$[PtCl_2(C_2H_4)$-(isoquinoline)]. In general, then, the ^{1}H nmr spectra of fresh $CDCl_3$ solutions of complexes **1**, prepared by reaction (1), show no $^3J_{Pt-NCH}$ but on standing, the small quantity of free ligand, which invariably precipitates along with the complexes, is removed by formation of *trans*-$[PtCl_2(L)_2]$ and the aged solutions then show $^3J_{Pt-NCH}$. At the present time we estimate that the free pyridine precipitated along with the complex $[PtCl_2(C_2H_4)(C_5H_5N)]$ is present to the extent of about 2 mole percent; this quantity of impurity cannot be ascertained from the usual ultimate analysis.

The observation of $^3J_{Pt-NCH} \simeq 40$ Hz. in the ^{1}H nmr spectra of **2** indicates that, if exchange is occurring, it must be slow on the nmr time scale; in particular, the life-time of the complex must be greater than about 0.025 sec in $CDCl_3$. It was of importance to ascertain whether the coupling could still be observed in the presence of very small quantities of free pyridine. For this purpose, 0.5 ml of a 0.54 *M* $CDCl_3$ solution of *trans*-$[PtCl_2(C_2H_4)$(pyridine)] was extracted with HBF_4 to remove free pyridine and to this solution was added 23 μl of a 0.12 *M* $CDCl_3$ solution of pyridine. The ^{1}H nmr spectrum of this solution which contained at least one mole percent free ligand still showed $^3J_{Pt-NCH}$. Thus it is possible to observe coupling in the presence of very small quantities of free pyridine. The $^3J_{Pt-NCH}$ is lost if 1.3 mole percent or more of pyridine is added. In another experiment designed to test the effect of small quantities of free olefin, a 0.5 ml sample of the HBF_4 extracted solution was treated with 5 μl of a 0.45 *M* $CDCl_3$ solution of dodecene and the ^{1}H nmr spec-

TABLE I

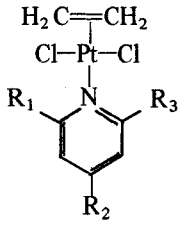
^{1}H NMR Spectral Results with  in $CDCl_3$ [a]

Sample (°C)	$H_{(\alpha)}$	$^3J_{195\,Pt-NCH}$	$H_{(\gamma)}$	$C_2H_4(H_a)$	$^2J_{195\,Pt-CH}$
Aged (30)	8.51	36	7.54	4.88	60
Fresh (30)	8.51	–	7.53	4.88	60
Fresh (–20)	8.50	36	–	4.89	60

[a] 90 MHz instrument, all chemical shift data in units of δ (from internal $CHCl_3$ (7.27) standard), and coupling data in Hz.

trum still showed $^2J_{Pt-CH}$ although the signal was broadened. These experiments show that ligand exchange via the solvolytic pathway in $CDCl_3$ is very slow and that $J\,|\,^{195}Pt - {}^1H\,|$ can still be observed in the presence of very small quantities of free ligands.

It is likely that steric interactions are maximized when there is substitution at the α position of the pyridine. If the substituent groups are sufficiently bulky to hinder exchange with adventitious free ligand, coupling should be observed immediately upon solution in $CDCl_3$. The effect of steric hinderance on exchange was investigated by preparing compounds 3*a*–3*e*.



	R_1	R_2	R_3
(*a*)	CH_3	H	H
(*b*)	C_2H_5	H	H
(*c*)	$PhCH_2$	H	H
(*d*)	$CH_3O(CH_2)_2$	H	H
(*e*)	CH_3	CH_3	CH_3

3

Examination of the ^1H nmr spectra of $CDCl_3$ solutions of complexes 3*a* and 3*b* at room temperature showed no $^3J_{Pt-NCH}$ initially, but after standing several days, coupling was observed. However complexes 3*c* and 3*d* showed coupling at room temperature immediately after their solution in $CDCl_3$ and 3*e* showed similar coupling behavior with the α methyl protons. The resistance of 3*e* to exchange has been demonstrated before.[4]

II. Ligand Trading

It has been shown previously[3] that mixing freshly prepared $CDCl_3$ solutions of complexes 2*b* and 2*j*, immediately resulted in the formation of two additional complexes, 2*e* and 2*i*. The complexes 2*b* and 2*e* are easily distinguished by virtue of the different chemical shifts of their ethylene protons. The presence of four complexes can be explained by any of three reactions: olefin trading only; pyridine trading only; or trading of both olefin and pyridine. Since the H_α protons of the pyridine moiety were not coupled to the ^{195}Pt and the olefin coupling to the ^{195}Pt was always present, it was assumed that pyridine trading rather than olefin trading occurred. Because we have now developed a procedure for removing free pyridine, a trading experiment was reinvestigated. Fresh $CDCl_3$ solutions of equimolar amounts of 2*a* and 2*g* were separately extracted with HBF_4 ($^3J_{Pt-NCH}$ present) and then mixed. The ^1H nmr spectrum clearly showed a signal for ethylene protons of the new complex 2*d* at room temperature, and furthermore, the olefins as well as the pyridines remained coupled to ^{195}Pt. Thus it would appear that when the free base is removed, trading still occurs but is apparently slower than when free base is present.

In an attempt to determine whether in reaction (3), it is the olefins or the pyridines which are trading, Scheme I was devised and complexes 4*a* and 2*k* were mixed:

$$\textit{trans}\text{-}[PtBr_2(C_2H_4)(4\text{-}CH_3C_5H_4N)] + \underset{4(a)}{} \quad \textit{trans}\text{-}[PtCl_2(\textit{cis}\text{-}C_4H_8)(C_5H_5N)] \quad \underset{2(k)}{}$$

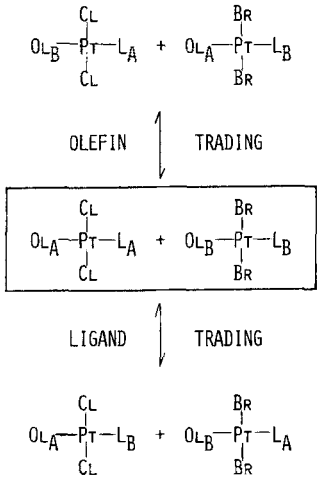
If the olefins traded, then the two new complexes formed should be 4*d* and 2*a*:

$$\textit{trans}\text{-}[PtBr_2(\textit{cis}\text{-}C_4H_8)(4\text{-}CH_3C_5H_4N)] \text{ and } \underset{4(d)}{} \quad \textit{trans}\text{-}[PtCl_2(C_2H_4)(C_5H_5N)]\,; \quad \underset{2(a)}{}$$

whereas if only the pyridines traded, the two new complexes formed should be 4*b* and 2*i*:

$$\textit{trans}\text{-}[PtBr_2(C_2H_4)(C_5H_5N)] \text{ and } \underset{4(b)}{} \quad \textit{trans}\text{-}[PtCl_2(\textit{cis}\text{-}C_4H_8)(4\text{-}CH_3C_5H_4N)] \quad \underset{2(i)}{}$$

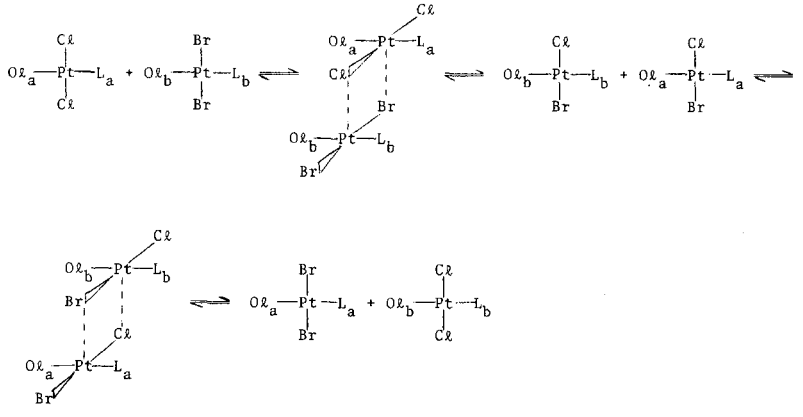
Finally, the presence of four new complexes, 2*a*, 2*i*, 4*b*, and 4*d* would indicate that both olefin and pyridine trading occurred. When the experiment was conducted, not only were the ethylene complexes 4*a*, 4*b*, and 2*a* observed, but three additional ethylene complexes were formed corresponding to $[PtClBr(C_2H_4)(C_5H_5N)]$, 5*a*, $[PtClBr(C_2H_4)(4\text{-}CH_3C_5H_4N)]$, 5*b*, and *trans*-$[PtCl_2(C_2H_4)(4\text{-}CH_3C_5H_4N)]$, 2*b*, giving a total of six ethylene complexes in approximately the statistical quantities expected for an equilibrium constant of one. The ethylene signals of the complexes 2*a*, 2*b*, 4*a*, 4*b* prepared *in situ* in the above experiment were identical to the ethylene signals of authentic samples of each. Although authentic samples of 5*a* and 5*b* were not prepared, the chemical shifts for the ethylene signals were reasonable for mixed halide complexes. In order to independently verify the



SCHEME I. TRADING OF OL'S ONLY, OR L'S ONLY.

The trading of halogens can be rationalized by assuming a series of bridging intermediates similar to those proposed elsewhere[5] and shown in Scheme II.

Scheme II depicts halogen trading only, leaving the Ol–Pt–Py moiety intact. But the trading experiments showed that either the olefin partners or the pyridine partners, or both, must also trade. Because olefins impart a large kinetic *trans* effect, solvolysis of the pyridine moiety followed by pyridine exchange would seem to be a reasonable set of reactions. Solvolysis of the olefin ligand seemed less likely but in order to determine if olefin trading can occur in $CDCl_3$ solutions, the following experiment was performed. Equimolar $CDCl_3$ solutions of $[Rh(C_2H_4)_2(acac)]$ and $(n\text{-}C_4H_9)_4N[PtCl_3(trans\text{-}C_4H_8)]$ were mixed. The ^1H nmr spectrum of the solution showed the gradual (30 min) buildup of $(n\text{-}C_4H_9)_4N[PtCl_3(C_2H_4)]$ indicating trading of olefins. This experiment was modeled after a similar one performed in ethanol[6], which demonstrated ethylene-ethylene trading.



SCHEME II. HALOGEN TRADING REACTION

formation of mixed halide complexes, equimolar $CDCl_3$ solutions of **2***a* and **4***b* were mixed. A new ethylene signal appeared in the ^1H nmr spectrum corresponding, as expected, to structure **5***a*. The entire solution was then evaporated to dryness and the ir of the residue determined. Two Pt–Cl bands appeared; one at 340 cm^{-1} assigned to **4***a*, and a band at 334 cm^{-1} which we assign to the Pt–Cl *trans* to Br.

At the present time we cannot decide whether only olefins, or only pyridines, or whether both types trade. Because both of these ligand moieties remain coupled to the platinum during the mixing of complexes, the steady state concentrations of free Ol and free L must be less than about 1.6 mole percent for the olefin and less than about 1 mole percent for the pyridine. If both ligand types are exchanging, their concentration must be sufficiently large to cause

the exchange. Whether solvolysis can provide these concentrations is not known, and further work is in progress.

Experimental Section

Infrared spectra were determined on either a Perkin-Elmer 337 or a Beckman IR-12 spectrometer using polystyrene, CO_2 and H_2O respectively, as standards. The ^1H nmr spectra were determined with either the Varian A-60 or T-60 or the Brucker HFX-90 instrument. Melting points were determined using the Fisher-Johns apparatus and are corrected. All solvents were reagent or spectral grade and were dried over molecular sieves. The pyridines were distilled just prior to use.

The known[3] procedures for preparing complexes 2, *trans*-(olefin)$PtCl_2$(L), were used to prepare complexes 3 and 4. Previously unreported complexes are described below.

1,3-Dichloro-2-ethylene-4(2-methylpyridine) platinum(II), 3*a*. To 200 mg (0.54 mm) of Zeise's salt dissolved in 3 ml of cold water, there was slowly added 0.96 ml (0.54 mm) of 2-methylpyridine. A yellow precipitate formed immediately. The compound was filtered, recrystallized from acetone-hexane, and dried; yield, 157 mg (75%). *Anal.* Calcd for $C_8H_{11}Cl_2NPt$: C, 24.81; H, 2.84. Found: C, 24.91; H, 3.02; ^1H nmr ($CDCl_3$), 4.81 (t, 4, $^2J_{Pt-CH}$ 60 Hz, C_2H_4), 3.05 (t, 3, $^4J_{Pt-NCCH}$ 8 Hz, CH_3), 6.3 (m, 3); 8.35 (m, 1, $^3J_{HCH}$ 4 Hz, $^3J_{Pt-NCH}$ 32 Hz).

The complex 3*b*, m.p. 83°, was prepared in 79% yield as above using 2-ethylpyridine. *Anal.* Calcd for $C_9H_{12}Cl_2NPt$: C, 26.93; H, 3.24; Pt, 48.7. Found: C, 27.18; H, 3.29; residue 46.1; ^1H nmr ($CDCl_3$), 1.32 (t, 3, $^3J_{HCH}$ 7 Hz, CH_3); 2.85 (m, 2, $^3J_{HCH}$ 7 Hz, $^4J_{Pt-NCCH}$ 4 Hz, CH_2); 4.83 (t, 4, $^2J_{Pt-CH}$ 62 Hz, C_2H_4); 6.3 (m., 3); 8.62 (m, 1, $^3J_{HCH}$ 5 Hz, $^3J_{Pt-NCH}$ 32 Hz).

The complex 3*c* was prepared as above, using 2-benzylpyridine; yield 190 mg (79%), m.p. 95–97°. *Anal.* Calcd for $C_{14}H_{15}Cl_2NPt$: C, 36.37; H, 3.23; Pt, 42.12. Found: C, 36.02; H, 3.21; residue, 43.8; ^1H nmr ($CDCl_3$), 4.10 (t, 2, $^4J_{Pt-NCCH}$ 4 Hz, CH_2), 4.80 (t, 4, $^2J_{Pt-CH}$ 62 Hz, C_2H_4), 8.6 (m, 3, CH=CHCH), 8.70 (m, 1, $^3J_{HCH}$ 6 Hz, $^3J_{Pt-NCH}$ 28 Hz).

Complex 3*d* was prepared as above in 73% yield using 2-methoxyethylpyridine. *Anal.* Calcd for $C_{10}H_{15}Cl_2NPt$: C, 27.84; H, 3.48; Pt, 45.2. Found: C, 27.70; H, 3.42; residue 42.5; ^1H nmr ($CDCl_3$), 3.37 (s, 3, CH_3O), 3.65 (m, 4, CH_2CH_2O), 4.88 (t, 4, $^2J_{Pt-CH}$ 62 Hz, C_2H_4), 8.5 (m, 3, CH=CHCH), 8.70 (m, 1, $^3J_{HCCH}$ 5 Hz, $^3J_{Pt-NCH}$ 32 Hz).

1,3-Dichloro-2-ethylene-4(3,5-dimethylpyridine) platinum(II) was prepared as above in 81% yield, m.p. 125°. *Anal.* Calcd for $C_9H_{13}Cl_2NPt$: C, 26.93; H, 3.24; Pt 48.6. Found: C, 27.12; H, 3.33, residue 48.3; ^1H nmr ($CDCl_3$), 3.05 (s, 6, CH_3), 4.88 (t, 4, $^2J_{Pt-CH}$ 60 Hz, C_2H_4), 7.53 (s, 1, CH), 8.51 (t, 2, $^3J_{Pt-NCH}$ 36).

Preparation of $K[PtBr_3(C_2H_4)]$. To 4 g of $K[PtCl_3(C_2H_4)]$ dissolved in 200 ml of H_2O was added 20 g of KBr dissolved in 50 ml H_2O. The mixture was shaken for 3 days under 3 atm of ethylene. The H_2O solution was then evaporated to dryness under reduced pressure and the resulting solid treated with three 200 ml portions of acetone. The acetone solution was evaporated to dryness under reduced pressure leaving an orange-yellow solid. This solid was dissolved in 200 ml H_2O and 20 g of KBr dissolved in 50 ml H_2O was added. The mixture was shaken for 3 more days under 3 atm of ethylene. The H_2O solution was worked up as above and the resulting orange solid, $K[PtBr_3(C_2H_4)]$, was used without recrystallization in the preparation of the following complexes.

1,3-Dibromo-2-ethylene-4-pyridine-platinum(II): To 0.500 g (0.099 mmoles) of $K[PtBr_3(C_2H_4)]$ dissolved in 10 ml of H_2O was added with stirring 0.1 ml (0.099 mmoles) of pyridine in 5 ml of H_2O. The orange-yellow solid which precipitated immediately was filtered, dried and recrystallized from $CHCl_3$/hexane. *Anal.* Calcd. for $C_7H_9NPtBr_2$: C, 18.19; H, 1.92. Found: C, 18.19; H, 1.96; ^1H nmr ($CDCl_3$), 5.05 (t, 4, $^2J_{Pt-CH}$ 61 Hz, (C_2H_4)); 8.94 (m, 2, $^3J_{Pt-NCH}$ 36 Hz); 7.49 (m, 2); 7.91 (m, 1).

1,3-Dibromo-2-ethylene-4-(4-methylpyridine) platinum(II). To 0.500 g (0.099 mmoles) of $K[PtBr_3(C_2H_4)]$ dissolved in 10 ml H_2O was added with stirring 0.1 ml (0.098 mmoles) of 4-methylpyridine in 5 ml H_2O. The orange-yellow solid which precipitated immediately was filtered, dried, and recrystallized from $CHCl_3$/hexane. *Anal.* Calcd for $C_8H_{11}NPtBr_2$: C, 20.18; H, 2.33. Found: C, 20.37; H, 2.27; ^1H nmr ($CDCl_3$), 5.03 (t, 4, $^2J_{Pt-CH}$ 61, Hz); 8.88 (m, 2, $^3J_{Pt-NCH}$); 7.31 (m, 2).

Reaction of *trans*-$[PtCl_2(Ol_a)(L_a)]$ with *trans*-$[PtCl_2(Ol_b)(L_b)]$. 0.250 g of *trans*-$[PtCl_2$(*cis*-2-C_4H_8)(C_5H_5N)] was dissolved in 0.5 ml of $CDCl_3$ and shaken with 0.5 ml of aqueous HBF_4. The aqueous layer was then separated from the $CDCl_3$ solution. This extraction procedure was repeated five times. Similarly, 0.250 g of *trans*-$[PtCl_2$

$(C_2H_4)(4\text{-}CH_3C_5H_4N)]$ dissolved in 0.5 ml of $CDCl_3$ was treated with HBF_4. The extracted $CDCl_3$ solutions of the two complexes were mixed and a ^1H nmr spectrum was taken within 5 min. ^1H nmr ($CDCl_3$) 4.92 (t, 4, $^2J_{Pt-CH}$); 4.89 (t, 4, $^2J_{Pt-CH}$). The same procedure was followed for the reaction of *trans*-$[PtCl_2(C_2H_4)(C_5H_5N)]$ with *trans*-$[PtBr_2(C_2H_4)(C_5H_5N)]$: ^1H nmr ($CDCl_3$), 5.04 (t, 4, $^2J_{Pt-CH}$); 4.92 (t, 4, $^2J_{Pt-CH}$) and *trans*-$[PtCl_2(cis\text{-}C_4H_8)(C_5H_5N)]$ with *trans*-$[PtBr_2(C_2H_4)(4\text{-}CH_3C_5H_4N)]$. ^1H nmr ($CDCl_3$); 5.05, 5.02, 4.97, 4.95, 4.92, 4.89 (t, 4, $^2J_{Pt-CH}$ 60 Hz for all six signals).

Reaction[6] of $Rh(C_2H_4)_2(acac)$ with $(n\text{-}C_4H_9)_4N[PtCl_3\text{-}(trans\text{-}C_4H_8)]$. To 0.35 g of $Rh(C_2H_4)_2(acac)$ in 0.5 ml of $CDCl_3$ was added to 0.155 g of $(n\text{-}C_4H_9)_4N[PtCl_3(trans\text{-}C_4H_8)]$ in 0.5 ml of $CDCl_3$. The solution was allowed to stand and the ^1H nmr spectrum determined intermittently. An ethylene signal at 4.91 δ grew in gradually and after 30 min the reaction appeared to reach equilibrium. ^1H nmr; 4.91 (t, 4, $^2J_{Pt-CH}$, 60 Hz); 3.58, 2.51.

ACKNOWLEDGEMENTS

The authors wish to thank Engelhard Industries, Inc. for a generous supply of platinum and the Reilly Tar and Chemical Company for samples of pyridines. We are grateful to the Atlantic Richfield Corp. for fellowships to L. S., F. P., and to Professor Fred Kaplan for helpful discussions concerning ^1H nmr interpretations.

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