C,N-Chelated (2-Pyridylmethyl)rhodium(III) Complexes and a Novel Dinuclear Rhodium(III) Complex Containing a 2,6-Dimethylpyridine-α,α'-diyl Group as an $\eta^2(C,N):\eta^3(C,C',N)$-Bridging Ligand

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(Received June 8, 1994)

Oxidative-addition reactions of excess 2-(chloromethyl) and 2,6-bis(chloromethyl)pyridines with [RhCl(PPh$_3$)$_3$] in toluene at room temperature afforded (2-pyridylmethyl)- and {2-(6-chloromethyl)pyridylmethyl}rhodium(III) complexes, *cis*(*PP*)-[RhCl$_2${C$_5$H$_3$(6-R)N-2-CH$_2$}(PPh$_3$)$_2$] (R=H, **1**-*cis*; R=CH$_2$Cl, **2**-*cis*), respectively, which isomerized to the corresponding *trans*(*PP*) complexes at elevated temperature. In refluxing toluene, the reactions thus resulted in the *trans*(*PP*) complexes (R=H, **1**-*trans*; R=CH$_2$Cl, **2**-*trans*) exclusively. A novel dinuclear rhodium(III) complex [Rh$_2$Cl$_4${C$_5$H$_3$N-2,6-(CH$_2$)$_2$}(PPh$_3$)$_2$], in which the 2,6-dimethylpyridine-α,α'-diyl ligand is *C,N*-chelated to one rhodium atom and bound to the second one in an η^3-pseudo-1-azaallylic fashion, was obtained by reactions of 2,6-bis(chloromethyl)pyridine with [RhCl(PPh$_3$)$_3$] (1:2 in mole) and of the **2**-*cis* with [RhCl(PPh$_3$)$_3$] (1:1 in mole), both in refluxing toluene. These were characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy and mass spectrometry as well as an elemental analysis and a molecular-weight determination.

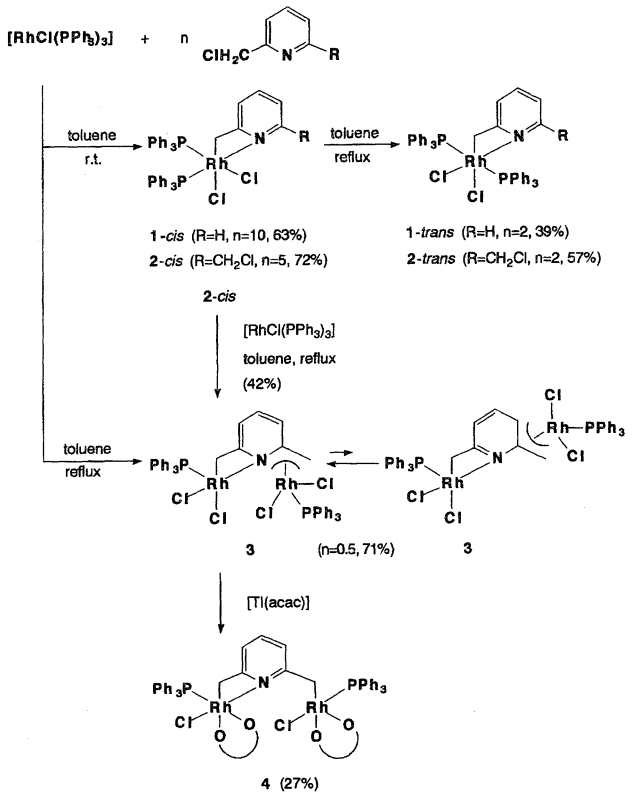
The oxidative addition of 2-(chloromethyl)pyridine to [Pd(PPh$_3$)$_4$] readily occurred in benzene[1] or toluene[2] to afford a 2-pyridylmethyl-bridged dinuclear complex of palladium(II) [{PdCl(μ-C$_5$H$_4$N-2-CH$_2$)(PPh$_3$)}$_2$], analogous to that obtained with 2-chloropyridine.[3] In the case of 2,6-bis(chloromethyl)pyridine, which is potentially bifunctional in oxidative addition reactions, however, the 2,6-dimethylpyridine-α,α'-diyl-bridged tetranuclear complex of palladium(II) [{Pd$_2$Cl(μ-Cl)-[μ-C$_5$H$_3$N-2,6-(CH$_2$)$_2$](PPh$_3$)$_2$}$_2$] was obtained in addition to the dinuclear complex [{PdCl[C$_5$H$_3$(6-CH$_2$Cl)N-2-CH$_2$](PPh$_3$)}$_2$].[4] These results have aroused interest in extending our studies to group-9 transition metals.

This paper reports on the preparation, characterization, and some reactions of mononuclear 2-pyridylmethyl and 2-(6-chloromethyl)pyridylmethyl complexes of rhodium(III), and of a dinuclear complex containing a 2,6-dimethylpyridine-α,α'-diyl group as a bridging ligand.

Results and Discussion

***C,N*-Chelated *Cis*(*PP*) Complexes.** When Wilkinson's complex [RhCl(PPh$_3$)$_3$] was allowed to react with an excess of 2-(chloromethyl)pyridine in toluene at room temperature, *cis*(*PP*)-[RhCl$_2$(C$_5$H$_4$N-2-CH$_2$)(PPh$_3$)$_2$] (**1**-*cis*) was first isolated as a kinetically controlled product. Under similar conditions, a controlled oxidative addition of one terminus of 2,6-bis(chloromethyl)pyridine to [RhCl(PPh$_3$)$_3$] afforded *cis*(*PP*)-[RhCl$_2${C$_5$H$_3$(6-CH$_2$Cl)N-2-CH$_2$}(PPh$_3$)$_2$] (**2**-*cis*). These are represented in Scheme 1.

In contrast with palladium(II),[1—4] rhodium(III) complexes, **1**-*cis* and **2**-*cis*, are monomeric in dichloromethane. The ^{1}H NMR spectrum of **1**-*cis* in CDCl$_3$ showed two methylene proton signals at $\delta=2.35$ and 2.58. The higher field signal is a doublet of doublets and the lower field one a doublet, both having the same coupling constant of 11.6 Hz. Irradiation at the frequency of the doublet of doublets reduced the lower field doublet to a singlet, and irradiation at the latter frequency reduced the doublet of doublets to a doublet, confirming the geminal coupling ($J=11.6$ Hz) of the methylene protons. Thus, only one of the two methylene protons couples to ^{31}P with $^3J_{PH}=5.5$ Hz, which is less than ca. 9 Hz in [{PdCl(μ-C$_5$H$_4$N-2-CH$_2$)(PPh$_3$)}$_2$].[2] In the spectrum of **2**-*cis* in CDCl$_3$, the corresponding methylene proton signals at $\delta=2.44$ and 2.50 are somewhat broad, and the geminal coupling constant and the coupling constant with ^{31}P are not proved. On the other hand, chloromethyl proton signals appeared at $\delta=4.20$ and 5.10 as an AB quartet, suggesting that the uncoordinated chloromethyl group becomes diastereotopic upon N-coordination. Thus, **2**-*cis*, and probably **1**-*cis*, too, constitute six-coordination by two chlorines, two



Scheme 1.

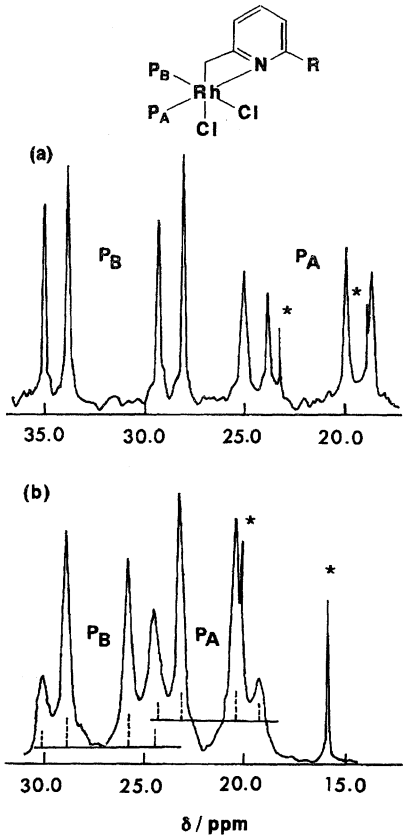


Fig. 1. The $^{31}P\{^1H\}$ NMR (ABX, X=^{103}Rh) spectra of (a) **1**-*cis* and (b) **2**-*cis* in CD_2Cl_2 at 24.2 MHz. δ denotes ppm from external standard H_3PO_4. Asteriscs show the signals for **1**-*trans* and **2**-*trans* with expanded intensities.

phosphines, and one *C,N*-chelation. The broadening of the H^6 pyridine-ring proton signal, which is observed in the ^1H NMR spectrum of **1**-*cis*, is due to coupling with both the vicinal proton and ^{31}P, and suggests that one of the two phosphorus atoms is situated in the position *trans* to the coordinated N atom.[5]

The phosphorus–phosphorus *cis* arrangement of these six-coordinate, octahedral complexes has been revealed by their $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra as follows. The $^{31}P\{^1H\}$ NMR spectra (Fig. 1) of **1**-*cis* and **2**-*cis* in CD_2Cl_2 exhibited simple and complex ABX (X=^{103}Rh) spin systems, respectively, thus confirming a *cis* configuration of the bis(phosphine) ligands. In the spectrum of **1**-*cis* (Fig. 1a), the lower field signal at δ=31.6 (P_B, $^1J_{RhP}$=137 Hz, $^2J_{PP}$=29.3 Hz) is sharp, while the higher field one at δ=22.0 (P_A, $^1J_{RhP}$=122 Hz) is somewhat broad. The appearance of the latter broad signal is probably due to the effect of the quadrupole moment of the nitrogen nucleus *trans* to P_A, thus making clear the assignment of that to the ^{31}P *trans* to N and, hence, the former to the ^{31}P *trans* to Cl. The $^{13}C\{^1H\}$ NMR spectrum of **1**-*cis* in CD_2Cl_2 showed two sets of phenyl-ring carbon signals of the triphenylphosphine ligands. This appears to reflect a difference in the magnetic circumstances due to the different *trans*-ligating atoms, N and Cl, and, as a result, shows a phosphorus–phosphorus *cis* arrangement in the complex. One more possible *cis*(*PP*) isomer with *trans*(*ClCl*) is denied by the absence of the ν(Rh–Cl) bands, which are about 293—345 cm^{-1}, characteristic for chlorine *trans* to chlorine.[6] At the present stage of investigation, however, we can not discriminate two possible optical isomers, **A** and **B** (Chart 1).

***C,N*-Chelated *Trans*(*PP*) Complexes.** When a $^{31}P\{^1H\}$ NMR spectral change of **1**-*cis* in CD_2Cl_2 was followed at a probe temperature of 26 °C, two new signals gradually appeared at around δ=19 and 23 (see Fig. 1a), and their signal intensity increased with decreasing intensity of the signals for **1**-*cis*. This phenomenon suggests that the *cis*(*PP*)–*trans*(*PP*) isomerization occurs slowly at this temperature. In fact, thermodynamically stable *trans*(*PP*) complexes, **1**-*trans* and **2**-*trans*, were isolated from the reaction mixtures of $[RhCl(PPh_3)_3]$ and 2-(chloromethyl)- and 2,6-bis(chlo-

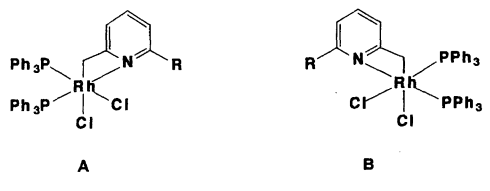


Chart 1.

romethyl)pyridines (both 1:2 in mole), respectively, in refluxing toluene, as represented in Scheme 1. The $^{31}P\{^1H\}$ NMR spectra of thus-obtained **1**-*trans* and **2**-*trans* in $CDCl_3$ showed a sharp doublet at $\delta=20.8$ and 17.6 respectively, both with the same coupling constant ($^1J_{RhP}=102$ Hz), which is reasonable for the *trans*(*PP*) arrangement.[7]

The *trans*(*PP*) octahedral structures of these complexes have a plane of symmetry consisting of the C, N, Cl, Cl, and Rh atoms, which is coplanar to the pyridine-ring. In the ^1H NMR spectra of the complexes in $CDCl_3$, methylene proton signals therefore appeared as a singlet for either the metal-coordinated methylene group or the 6-chloromethyl substituent in **2**-*trans*. The $^{13}C\{^1H\}$ NMR spectra of **1**-*trans* and **2**-*trans* also support their symmetrical structures. For example, the metal-coordinated methylene carbon and the pyridine-ring C^2 carbon each resonated as a singlet without *cis*-coupling to the ^{31}P nuclei. The spectra showed only one set of signals for the phenyl-ring carbons of the triphenylphosphine ligands. All of these data are in contrast to those for the *cis*(*PP*) complexes and appropriate for the *trans*(*PP*) geometry.

Dinuclear $\eta^2:\eta^3$-Bridging Complex. In the complex **2**-*cis* or **2**-*trans*, one of the originally attached chloromethyl groups remained unaltered. When this uncoordinated chloromethyl group in **2**-*cis* was forced to undergo a further oxidative addition in refluxing toluene, complex **3** was obtained as an orange product in medium yield. The same complex was also prepared in better yield by the direct reaction of 2,6-bis(chloromethyl)pyridine with $[RhCl(PPh_3)_3]$ (2:1 in mole) in refluxing toluene (Scheme 1). An elemental analysis and the cryoscopic and FAB mass spectral data have revealed its dinuclear formulation as being $[Rh_2Cl_4\{(C_5H_3N\text{-}2,6\text{-}(CH_2)_2\}(PPh_3)_2]$.

In the $C(\alpha),N,C(\alpha')$-bridging tandem tetranuclear palladium complex, in which the 2,6-dimethylpyridine-α,α'-diyl ligand was unsymmetrically bound to three metal atoms through two methylene carbons and a nitrogen atom, two sets of the metal-coordinated methylene proton signals were observed in the region of $\delta=2.0$—3.6 in its ^1H NMR spectrum in $CDCl_3$.[4] As shown in Fig. 2, the ^1H NMR spectrum of **3** in CD_2Cl_2 was temperature variant, suggesting that complex **3** is a stereochemically non-rigid in solution. The rigid spectrum of **3**, which was obtained at −60 °C, showed two sets of methylene proton signals, one set in the same region ($\delta=2.64$ dd, 3.28 d) as in the above-mentioned α,α'-diyl-palladium complex, but another set appearing in the lower field region ($\delta=3.79$ t, 4.24 br t). The fact that the latter chemical shifts are in the same region as in the syn and anti protons of the η^3-allyl- and 2-methylallylrhodium(III) complexes, $[RhCl_2(\eta^3\text{-allyl})L_2]$ (L=PPh_3[8] and pyridine[9]) and $[RhCl_2(\eta^3\text{-2-methylallyl})(PPh_3)_2]$,[8] suggests, that the bonding mode of the $RhCH_2\text{–}C_5H_3N\text{–}CH_2$ moiety to the second rhodium

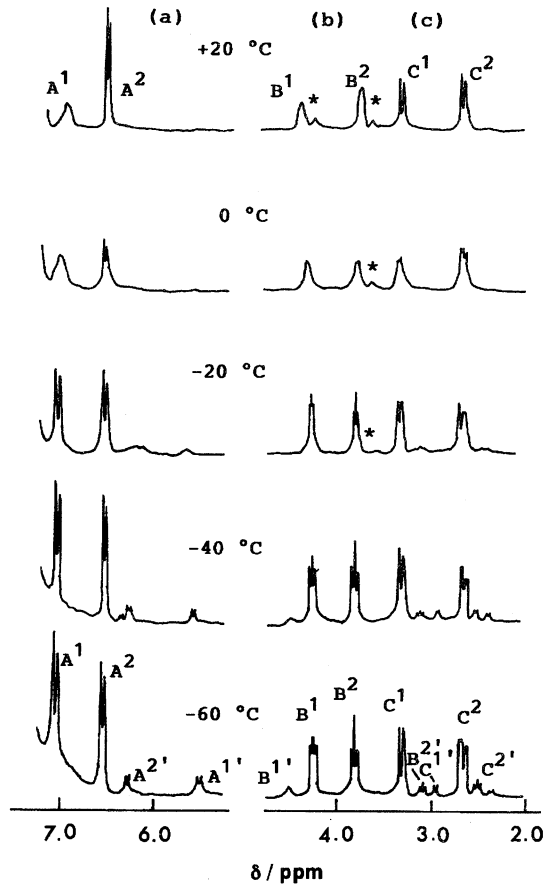


Fig. 2. The variable-temperature 400 MHz–^1H NMR spectra of **3** in CD_2Cl_2 in the regions of (a) pyridine-ring, (b) Rh–allyl, and (c) Rh–CH_2 protons. Non-prime and prime notations denote the signals for the η^3-pseudo-1-azaallyl and η^3-pseudo-allyl structures respectively. Asteriscs denote the signals for an unknown isomer.

atom is different from the σ-type, and rather appropriate for the η^3-pseudo-1-azaallylic or allylic fashion, such as the structures (**C**,**E** or **D**,**F**) shown in Chart 2. The

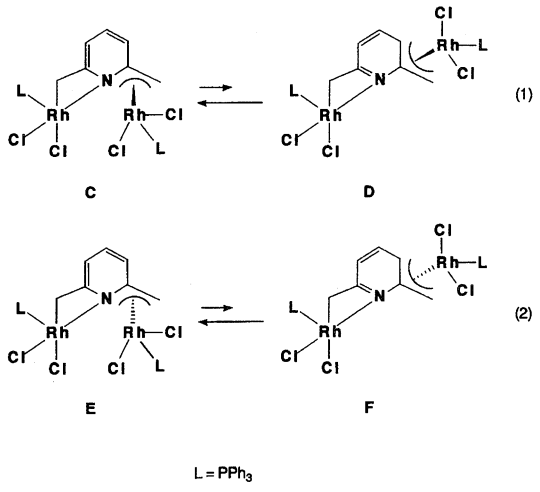


Chart 2. Possible optical isomers for complex **3**.

pyridine-ring proton signals showed two sharp doublets (δ=6.52 and 7.04 for H^3 and H^5 respectively) and one tripret (δ=7.27 for H^4) in the same region as in complexes **1** and **2** with a vicinal coupling of 7.7 Hz, implying that the predominant species at low temperatures is the η^3-pseudo-1-azaallyl complex. The spectrum at −60 °C, however, revealed the presence of at least one kind of minor species, which is denoted by the prime in Fig. 2. Upon increasing temperature, these signals for the major and minor species as a whole gradually broadened, some of the former signals becoming sharp again at 20 °C and the latter ones disappearing with coalescence before the temperature was raised to 0 °C. In general, two signals having a large chemical shift separation will coalesce more slowly than slightly separating signals. Based on this principle, we infer that (1) in the pyridine-ring proton region the protons denoted by A^1 and $A^{1'}$ interconvert, while A^2 and $A^{2'}$ also do so at the same time; (2) the allylic protons, B^1 and $B^{1'}$, as well as B^2 and $B^{2'}$, respectively, interconvert simultaneously; and (3) the σ-bonded methylene protons, C^1 and $C^{1'}$, as well as C^2 and $C^{2'}$ likewise interconvert. The drastic upfield shift of the pyridine-ring H^5 signal from A^1 to $A^{1'}$ is probably due to a shielding effect arising from binding of the pyridine-ring C^5 to the metal, suggesting the presence of dynamic processes, (1) and (2), such as those shown in Chart 2, namely, suprafacial shifts between η^3-*C*(α'), *C*(6), *N* and η^3-*C*(α'), *C*(6), *C*(5). As can be seen in Fig. 2, the equilibrium, (1) or (2), lies very far to the left, implying that the η^3-pseudo-1-azaallyl structure is thermodynamically more stable than the η^3-pseudo-allyl counterpart. Although several metal complexes having the η^3-aminoethylene-*C*,*C*′,*N* functionality have been prepared and studied for the transition metals of V,[10] Mo,[11] and Ru,[12] η^3-1-azaallyl complexes containing the pyridine-ring nitrogen atom as an allyl constituent element have been known only in lithium salts to our knowledge.[13] In this case, the metal atom was situated solely on the η^3-pseudo-1-azaallyl side.

As shown in Fig. 2, the signals of the syn and anti protons of **3** slightly broadened with increasing temperature, probably due to a suprafacial shift. However, the antarafacial shift from **C** to **E** (or **D** to **F**) of the $RhCl_2(PPh_3)$ unit through the intermediacy of a σ-bonded species did not occur up to 50 °C, since no indication of the coalescence of these signals was recognized, even at that temperature in $CDCl_3$. This is different from that of the ubiquitous η^3-allyl complex. Recently, Carmona and colleagues[14] reported on a suprafacial shift of the $NiBr(PMe_3)$ unit in the dinuclear pseudo-allyl nickel(II) complex *trans*-[$(Me_3P)BrNi(\mu$-$\eta^3:\eta^1$-$CH_2C_6H_4)NiBr(PMe_3)_2$] (*para*). However, no antarafacial shift of the $NiBr(PMe_3)$ unit through the σ-benzyl species has been observed for these *para* and *meta* complexes. This has been attributed to the electron-rich nature of the arylic $NiBr(PMe_3)_2$ substituent, which resulted in a decreased electrophilicity of the pseudo-allylic moiety, and, hence, in a reduced tendency to form reversibly, on the NMR time scale, a σ-benzylic species by the incorporation of a second molecule of the strongly basic PMe_3. In the present case, the $RhCH_2$ (allyl) carbon is surprisingly shielded (see bellow), suggesting that the picolyl $RhCl_2(PPh_3)$ substituent exerts the same effect to the pseudo-azaallyllic moiety. The steric hindrance for accepting two more phosphine molecules also inhibits the conversion of the moiety into a σ-bonded species. The signals denoted by asteriscs changed independently and colapsed with decreasing temperature. The structure of this minor species therefore remains unknown at the present stage.

The $^{13}C\{^1H\}$ NMR spectrum of **3** in CD_2Cl_2 at ambient temperature showed sharp signals, except for $RhCH_2$ (allyl), which appeared at δ=2.36 as a somewhat broad doublet. Two sets of PPh_3 signals (denoted by non-prime and prime notations in the Experimental section) were obviously recognized. Of these, only one set of the signals broadened along with a decrease in the temperature, and almost colapsed at −60 °C, supporting the non-rigidity of the (η^3-azaallyl)$RhCl_2(PPh_3)$ group in solution. However no rigid spectrum, was obtained, even at −90 °C, because of the widespread observational frequency-range for ^{13}C NMR. At −90 °C, each of the phenyl *ortho*, *meta*, and *para* carbon signals split in three in almost equal intensities with a still somewhat broad appearance. Although such splitting and broadening were also observed for the phenyl proton signals of **3** in the variable-temperature ^1H NMR spectra below −40 °C, these were not noticed in the ^{31}P NMR spectra. Therefore, the splitting into these three signals may be attributed to the sterically restricted rotation of the Rh–P bond in the (η^3-azaallyl)-$RhCl_2(PPh_3)$ unit at −90 °C. No appreciable broadening or splitting of the pyridine-ring C^5 signal was observed in the variable-temperature $^{13}C\{^1H\}$ NMR spectra of **3**.

To further confirm the η^3-allylic coordination of the $RhCH_2$–C_5H_3N–CH_2 moiety, we observed $^1J_{CH}$ of the terminal carbon. The value obtained at ambient temperature was 152 Hz, which is larger than 145 Hz for the *C*,*N*-chelated methylene carbon, indicating its higher sp^2 character. These values coincide with those for the η^3-allylic methylene and σ-bonded methylene carbons, i.e., 153 and 152 Hz for *trans*-[$(Me_3P)BrNi(\mu$-$\eta^3:\sigma$-$CH_2C_6H_4)NiBr(PMe_3)_2$] (*meta* and *para*)[14] and 142 Hz for *trans*, *trans*-[$(Me_3P)_2BrNi(\mu$-$\sigma:\sigma$-*m*-$CH_2C_6H_4)$-$NiBr(PMe_3)_2$].[14]

Figure 3 shows the variable-temperature 160 MHz-$^{31}P\{^1H\}$ NMR spectra of **3** in CD_2Cl_2. The spectrum at ambient temperature was simplest and revealed the presence of two independent species denoted by A^1–A^2 [δ=36.3 d (A^1)–45.0 d (A^2)] and X^1–X^2 [δ=35.7 d (X^1)–45.4 d (X^2)], with a relative intensity of about

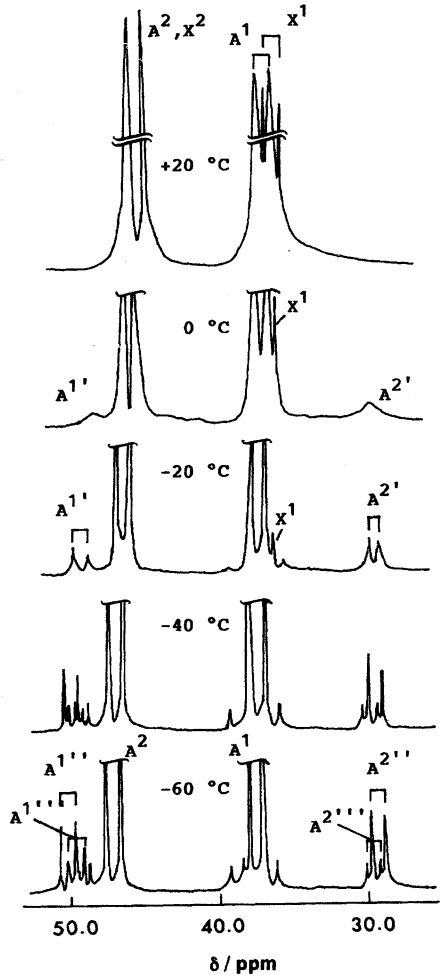


Fig. 3. The variable-temperature 160 MHz-^{31}P-{^{1}H} NMR spectra of **3** in CD_2Cl_2. Non-prime and prime (single, double and triple) A^1–A^2 notations denote the signals for the η^3-pseudo-1-azaallyl and η^3-pseudo-allyl complexes respectively. X^1–X^2 represents the signals for an unknown isomer. On numerical notations 1 and 2, see Chart 3.

3:1. The latter species presumably coincides with the unknown isomer observed in the ^{1}H NMR spectrum of **3** at 20 °C. Upon decreasing the temperature, each signal repeated its splitting; the final rigid spectrum, which was obtained at −60 °C, revealed the presence of at least three kinds of isomeric species and other species originated from X^1–X^2 [δ=37.1 d (A^1)–46.7 d (A^2), 49.7 d ($A^{1''}$)–29.0 d ($A^{2''}$), 49.2 d ($A^{1'''}$)–29.3 d ($A^{2'''}$), 38.5 d ($X^{1'}$)–48.8 d ($X^{2'}$) and ? ($X^{1''}$)–36.2 d ($X^{2''}$)]. As represented by A^1–A^2, $A^{1'}$–$A^{2'}$ and so on, two phosphine atoms of each set do not mutually couple, implying that their respective phosphines coordinate to the different metal atoms. When we consider these spectral change based on the previously noted principle, the way in which their signals mutually coalesce with increasing temperature is proved. Thus, (1) the species A^1–A^2 is invariably present in solution as a major product; (2) both the signals denoted by $A^{1''}$–$A^{2''}$ and $A^{1'''}$–$A^{2'''}$ in the spectrum at −60 °C coalesce at −20 °C into the broad signals of $A^{1'}$–$A^{2'}$; (3) then, the $A^{1'}$–$A^{2'}$ signals coalesce into A^1–A^2 at ambient temperature to give a sharp (A^2) and rather broad (A^1) doublets. It appears to be difficult to discriminate distinctly between the η^3-pseudo-1-azaallyl and η^3-pseudo-allyl structures of **3** by its ^{31}P NMR data, since the structures will not produce marked differences in their chemical shifts and couplings. However, we can tentatively assign the $A^{1'}$–$A^{2'}$ signals, which coalesce into A^1–A^2 for the major η^3-pseudo-1-azaallyl isomer **C** or **E**, to the η^3-C(α'), C(6), C(5)-pseudo-allyl isomer **D** or **F**. This could be consistent with the ^{1}H NMR data of **3**.

Chart 3 shows a correlation for the structures regarding the chemical shifts (δ) and coupling constants (J). The conversion of structure **C** to **D** (or **E** to **F**) causes a shielding of the phosphorus nucleus attached to Rh^2 and weakens the P–Rh^2 bond, due to increasing basicity of the pyridine nitrogen atom. On the contrary, the same conversion may result in a deshielding of the phosphorus atom on Rh^1 and in a strengthening of the P–Rh^1 bond. It is not clear at the present stage of investigation whether the ligand arrangement around the metal atoms shown in Chart 3 is correct or not. In any event, the result of this correlation reinforces the validity of the supposed $\eta^2(C,N):\eta^3(C,C',N)$-bridging structure of **3**. The preference of **C** to **E**, or vice versa, remains unknown.

The absence of the antarafacial shift of **C** to **E** via a σ-bonded intermediate was also confirmed by the addition of triphenylphosphine. For example, when one-tenth mole of triphenylphosphine was added to the solution, no fundamental change was observed for its vari-

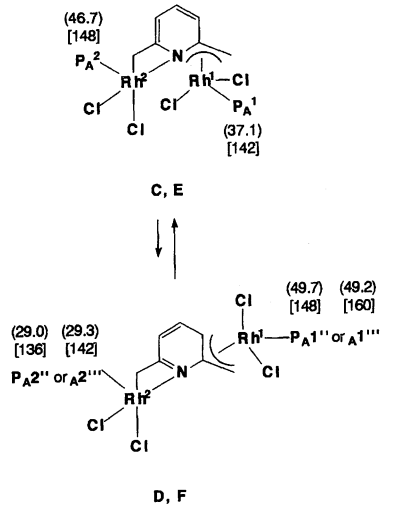


Chart 3. A correlation for the η^3-pseudo-1-azaallyl structures **C**,**E**, and the η^3-pseudo allyl structures **D**,**F** as for the chemical shifts (δ/ppm) and the coupling constants [J/Hz]. Double and triple prime notations discriminate the different arrangements of the three unidentate ligands around the metal.

able-temperature ^{1}H and ^{31}P{^{1}H} NMR spectra, except that the η^3-*C,C,C*/η^3-*C,C, N* isomer ratio increased to some extent (^{1}H and ^{31}P) and the signal for free PPh_3 appeared newly at around $\delta=0$ (^{31}P).

Dinuclear $\eta^2:\eta^1$-Bridging Complex. When four equivalents of thallium(I) pentane-2,4-dionate, [Tl(acac)], were allowed to react with complex **3** in dichloromethane at room temperature, only two of the four chloride ions were substituted by the pentane-2,4-dionate ligand to afford $[Rh_2Cl_2(acac)_2\{C_5H_3N\text{-}2,6\text{-}(CH_2)_2\}(PPh_3)_2]$ (**4**) in low yield. In contrast with **3**, the ^{1}H NMR spectrum of **4** in $CDCl_3$ was temperature invariant and showed two sets of the metal-coordinated methylene proton signals in the region of $\delta=1.8$—2.8, indicating that the η^3-1-azaallylic bond in **3** was converted to the Rh–C σ bond. The above formulation, which was determined by an elemental analysis and the cryoscopic data, predicts a symmetrical structure for complex **4**. However, all of the ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR data for **4** suggest an unsymmetrical structure such as that shown in Scheme 1. In addition to the presence of two sets of the metal-coordinated methylene proton signals, the ^{1}H NMR spectrum of **4** showed four methyl and two methyne signals from two pentane-2,4-dionate ligands. In the ^{13}C{^{1}H} NMR spectrum, four methyl, four carbonyl, and two methyne carbon signals were observed together with the two ill-defined methylene carbon signals. Interestingly, one of four methyl carbon signals couples with ^{31}P with $^4J_{CP}=7.3$ Hz, implying that one acetyl group exists in the position *trans* to P. The ^{31}P[^{1}H] NMR spectrum showed two distinct signals at $\delta=34.0$ and 37.3 with $^1J_{RhP}=137$ and 156 Hz, respectively.

Experimental

Unless otherwise stated, the reactions were performed under an atmosphere of nitrogen, using solvents which were redistilled under argon. Commercially available 2,6-bis(chloromethyl)pyridine was used without further purification. 2-(Chloromethyl)pyridine was freed from its hydrogen chloride adduct by the action of triethylamine. Wilkinson's complex $[RhCl(PPh_3)_3]$[15] and thallium(I) pentane-2,4-dionate[16] were prepared by the published methods.

Preparation of *cis*(*PP*)-[$RhCl_2(C_5H_4N\text{-}2\text{-}CH_2)(PPh_3)_2$)] (1-*cis*) and *cis*(*PP*)-[$RhCl_2\{C_5H_3(6\text{-}CH_2Cl)N\text{-}2\text{-}CH_2\}_2$] (2-*cis*). 2-(Chloromethy)pyridine (1.38 g, 10.8 mmol) was added to a suspension of [RhCl(PPh$_3$)$_3$] (1.00 g, 1.08 mmol) in toluene (40 cm^3), and the mixture was stirred at room temperature for 2 h. The dark red-violet suspension turned to a yellow suspension upon the reaction. The pale-yellow solid formed was filtered off, washed with diethyl ether (10 cm^3), then dried in vacuo.

The complex was recrystallized from dichloromethane–diethyl ether in air. The yield of 1-*cis*: 0.54 g (63%). No ν(Rh–Cl) bands, characteristic for chlorine *trans* to chlorine, are present in the region of about 293—345 cm^{-1}.[6] ^{1}H NMR ($CDCl_3$) $\delta=2.35$ (1H, dd, $J=11.6$ Hz, $^3J_{PH}=5.5$ Hz, RhC*H*H), 2.58 (1H, d, $J=11.6$ Hz, RhCH*H*), pyridine ring 6.45 (1H, d, $J=7.9$ Hz, H^3), 6.73 (1H, t, $J=7.9$ Hz, H^5), 8.01 (1H, br, H^6), 7.30 (1H, dt, $J=7.9$ and 1.2 Hz, H^4); ^{13}C NMR (CD_2Cl_2) $\delta=11.2$ (d, $^2J_{PC}=16.1$ Hz, RhC), pyridine ring 173.1 (d, $^3J_{PC}=4.4$ Hz, C^2), 122.8 (s, C^3), 136.5 (s, C^4), 122.1 (s, C^5), 145.2 (s, C^6), PPh_3 133.1 (d, $^1J_{PC}=48.4$ Hz, *i*-C), 131.0 (d, $^1J_{PC}=48.4$ Hz, *i*-C′), 135.4 (d, $^2J_{PC}=10.2$ Hz, *o*-C), 135.2 (d, $^2J_{PC}=10.3$ Hz, *o*-C′), 128.0 (d, $^3J_{PC}=10.2$ Hz, *m*-C), 127.8 (d, $^3J_{PC}=10.3$ Hz, *m*-C′), 130.5 (s, *p*-C and *p*-C′); ^{31}P NMR (CD_2Cl_2) $\delta=22.0$ (ABX spin system, X=^{103}Rh, $^1J_{RhP}=122$ Hz, $^2J_{PP}=29.3$ Hz, P$_A$), 31.6 ($^1J_{RhP}=137$ Hz, P$_B$). Found: C, 61.30; H, 4.52; N, 1.72%; Mol wt 800. Calcd for $C_{42}H_{36}Cl_2NP_2Rh$: C, 63.81; H, 4.59; N, 1.77%; M 791.

Similarly, complex **2**-*cis* was obtained using 2,6-bis(chloromethyl)pyridine (0.22 g, 1.3 mmol) and [RhCl(PPh$_3$)$_3$] (0.23 g, 0.25 mmol).

The yield of **2**-*cis*; 0.15 g (72%). No ν(Rh–Cl) bands, characteristic for chlorine *trans* to chlorine, are present in the region of about 293—345 cm^{-1}.[6] ^{1}H NMR ($CDCl_3$) $\delta=2.44$ (1H, br, Rh-C*H*H), 2.50 (1H, br, RhCH*H*), pyridine ring 6.43 (1H, d, $J=7.9$ Hz, H^3), 7.39 (1H, t, $J=7.9$ Hz, H^4), 4.20, 5.10 (2H, ABq, $J=15.3$ Hz, CH_2Cl); ^{13}C NMR (CD_2Cl_2) $\delta=12.7$ (d, $^2J_{PC}=16.1$, $^1J_{CH}=147$ Hz, RhC) 43.2 (s, $^1J_{CH}=156$ Hz, CH_2Cl), pyridine ring 173.1 (d, $^3J_{PC}=4.4$ Hz, C^2), 122.4 (s, C^3), 137.0 (s, C^4), 120.7 (s, C^5), 158.2 (s, C^6), PPh_3 $\delta=$ 130.6 (s, *p*-C), 130.4 (s, *p*-C′), other signals are not assigned because of the low resolution; ^{31}P NMR (CD_2Cl_2) $\delta=22.6$ (ABX spin system, X=^{103}Rh, $^1J_{RhP}=135$ Hz, $^2J_{PP}=29.0$ Hz, P$_A$), 26.5 ($^1J_{RhP}=129$ Hz, P$_B$). Found: C, 60.87, H, 4.46; N, 1.66%; Mol wt 852. Calcd for $C_{43}H_{37}Cl_3NP_2Rh$: C, 61.56; H, 4.45; N, 1.67%; M 839.

Preparation of *trans*(*PP*)-[$RhCl_2(C_5H_4N\text{-}2\text{-}CH_2)(PPh_3)_2$] (1-*trans*). 2-(Chloromethyl)pyridine (0.13 g, 1.0 mmol) and [RhCl(PPh$_3$)$_3$] (0.46 g, 0.50 mmol) were placed in a reaction vessel and toluene (70 cm^3) was added. The reaction mixture was refluxed with stirring for 2 h. A clear yellow solution was obtained just before the reflux, and then a pale-yellow precipitate began to deposit. After filtration the solid was discarded and the filtrate was concentrated under reduced pressure to deposit another pale-yellow precipitate, which was filtered off, washed with diethyl ether, then dried in vacuo. Yield: 0.15 g (39%). ^{1}H NMR ($CDCl_3$) $\delta=2.56$ (2H, s, $RhCH_2$), pyridine ring 6.16 (1H, d, $J=7.9$ Hz, H^3), 5.99 (1H, t, $J=7.9$, H^5), 6.54 (1H, d, $J=7.9$ Hz, H^6), 7.02 (1H, t, $J=7.9$ Hz, H^4); ^{13}C NMR ($CDCl_3$) $\delta=34.2$ (s, RhC), pyridine ring 172.8 (s, C^2), 122.7 (s, C^3), 134.2 (s, C^4), 121.1 (s, C^5), 146.7 (s, C^6), PPh_3 131.5 (t, $^1J_{PC}=22.8$ Hz, *i*-C), 134.8 (t, $^2J_{PC}=5.1$ Hz, *o*-C), 127.8 (t, $^3J_{PC}=4.4$ Hz, *m*-C), 129.6 (s, *p*-C); ^{31}P NMR ($CDCl_3$) $\delta=20.8$ (d, $^1J_{RhP}=102$ Hz). Found: C, 62.83; H, 4.50; N, 1.72%; Mol wt 851. Calcd for $C_{42}H_{36}Cl_2NP_2Rh$: C, 63.81; H, 4.59; N, 1.77%; M 791.

Preparation of *trans*(*PP*)-[$RhCl_2\{C_5H_3(6\text{-}CH_2Cl)N\text{-}2\text{-}CH_2\}(PPh_3)_2$] (2-*trans*). 2,6-bis(chloromethyl)pyridine (0.11 g, 0.60 mmol) and [RhCl(PPh$_3$)$_3$] (0.28 g, 0.30 mmol) were placed in a reaction vessel and toluene (40 cm^3) was added. The reaction mixture was refluxed with stirring for 2 h. A clear yellow solution was obtained just before the reflux; then, a yellow precipitate began to deposit. The reaction mixture was concentrated under reduced pressure to obtain an additional precipitate. The solid was filtered off, washed with diethyl ether, then dried in vacuo. The complex was recrystallyzed from dichloromethane–di-

ethyl ether in air. Yield: 0.14 g (57%). ^{1}H NMR ($CDCl_3$) δ=2.66 (2H, br s, $RhCH_2$), pyridine ring 6.29, 6.85 (2H, d, J=7.9 Hz, H^3 and H^5), 7.36 (1H, t, J=7.9 Hz, H^4), 2.88 (2H, s, CH_2Cl); ^{13}C NMR ($CDCl_3$) δ=31.3 (s, RhC) 42.5 (s, CH_2Cl), pyridine ring 160.9 (s, C^2), 121.9 (s, C^3), 133.7 (s, C^4), 119.6 (s, C^5), 135.5 (s, C^6), PPh_3 131.4 (t, $^1J_{PC}$=22.8 Hz, *i*-C), 134.8 (br, *o*-C), 127.9 (br, *m*-C), 129.9 (s, *p*-C); ^{31}P NMR ($CDCl_3$) δ=17.6 (d, $^1J_{RhP}$=102 Hz). Found: C, 61.54; H, 4.47; N, 1.67%; Mol wt 800. Calcd for $C_{43}H_{37}Cl_3NP_2Rh$: C, 61.56; H, 4.45; N, 1.67%; M 839.

Preparation of $[Rh_2Cl_4\{(C_5H_3N\text{-}2,6\text{-}CH_2)_2\}(PPh_3)_2]$ (3). Method A. A mixture of $[RhCl(PPh_3)_3]$ (0.47 g, 0.50 mmol) and 2,6-bis(chloromethyl)pyridine (0.04 g, 0.25 mmol) in toluene (50 cm^3) was refluxed with stirring for 2 h. An orange precipitate formed was filtered off, washed with diethyl ether, then dried in vacuo. The complex was recrystallized from dichloromethane–diethyl ether. Yield: 0.17 g (71%). ^{1}H NMR (CD_2Cl_2, −60 °C) δ=2.64 (1H, dd, J=12.2 Hz, $^3J_{PH}$=4.9 Hz, RhC*H*H), 3.28 (1H, d, J=12.2 Hz, RhCH*H*), (s and a denote *syn* and *anti* protons respectively) 3.79 (1H, t, $^2J_{H^SH^a}$=$^3J_{PH^S}$=6.6 Hz, H^a), 4.24 (1H, br t, H^S), pyridine ring 6.52 (1H, d, J=7.9 Hz, H^3), 7.04 (1H, d, J=7.9 Hz, H^5), 7.27 (1H, t, J=7.9 Hz, H^4); ^{13}C NMR (CD_2Cl_2) δ=2.36 (br d, $^2J_{PC}$=25.0, $^1J_{CH}$=152 Hz, $RhCH_2$ (allyl)), 13.6 (dd, $^2J_{PC}$=25.0 Hz, $^1J_{RhC}$=7.3, $^1J_{CH}$=145 Hz, $RhCH_2$), pyridine ring 174.2 (d, $^3J_{PC}$=5.9 Hz, C^2), 122.7 (s, C^3), 137.3 (s, C^4), 120.3 (s, C^5), 165.9 (s, C^6), PPh_3 129.9 (d, $^1J_{PC}$=55.8 Hz, *i*-C′), 134.7 (d, $^2J_{PC}$=8.8 Hz, *o*-C), 134.5 (d, $^2J_{PC}$=8.8 Hz, *o*-C′), 128.9 (d, $^3J_{PC}$=11.8 Hz, *m*-C), 128.4 (d, $^3J_{PC}$=11.8 Hz, *m*-C′), 131.9 (s, *p*-C), 131.1 (s, *p*-C′); (−90 °C) δ=0.9—1.1 (m, $RhCH_2$ (allyl)), 13.9 (dd, $^2J_{PC}$=17.6, $^1J_{RhC}$=4.4 Hz, $RhCH_2$); ^{31}P NMR (CD_2Cl_2, −60 °C) δ=37.1 (d, $^1J_{RhP}$=142 Hz, P_{A^1}), 46.7 (d, $^1J_{Rh'P}$=148 Hz, P_{A^2}), 49.7 (d, $^1J_{RhP}$=148 Hz, $P_{A^{1''}}$), 29.0 (d, $^1J_{Rh'P}$=136 Hz, $P_{A^{2''}}$), 49.2 (d, $^1J_{RhP}$=160 Hz, $P_{A^{1'''}}$), 29.3 (d, $^1J_{RhP'}$=142 Hz, $P_{A^{2'''}}$), ommitted for other species. FAB MS m/z 977 (M^+), 942 ($M-Cl^+$), 906 ($M-2Cl^+$), 506 ($M-3Cl-PPh_3-Rh^+$), 470 ($M-4Cl-PPh_3-Rh^+$). Found: C, 52.54; H, 3.80; N, 1.44%; Mol wt 978. Calcd for $C_{43}H_{37}Cl_4NP_2Rh_2$: C, 52.84; H, 3.82; N, 1.43%; M 977.3.

Method B. A mixture of complex **2**-*cis* (0.20 g, 0.24 mmol) and $[RhCl(PPh_3)_3]$ (0.22 g, 0.24 mmol) in toluene (60 cm^3) was refluxed with stirring for 2 h. An orange precipitate formed was treated in a similar manner as mentioned above. Yield: 0.098 g (42%).

Preparation of $[Rh_2Cl_2(acac)_2\{C_5H_3N\text{-}2,6\text{-}(CH_2)_2\}(PPh_3)_2]$ (4). A mixture of complex **3** (0.30 g, 0.31 mmol) and [Tl(acac)] (0.37 g, 1.2 mmol) in dichloromethane (50 cm^3) was stirred at room temperature for 5 h. The precipitated TlCl was filtered off and the filtrate was evaporated to dryness under reduced pressure. The residue was extracted with benzene (20 cm^3) and the yellow solution was concentrated. Hexane was added to the concentrate to deposit a yellow precipitate, which was filtered off, washed with hexane, then dried in vacuo. The product contained by-products in this stage and was recrystallized from dichloromethane–hexane. Yield: 0.09 g (27%). ^{1}H NMR ($CDCl_3$) δ=1.83 (1H, dd, J=11.6 Hz, $^3J_{PH}$=4.3 Hz, RhC*H*H), 2.53 (1H, dd, J=11.6 Hz, $^3J_{PH}$=3.1 Hz, RhCH*H*), 2.56 (1H, t, J=$^3J_{PH}$=11.6 Hz, Rh′C*H*H) 2.76 (1H, br, Rh′CH*H*), pyridine ring 6.32, 6.42 (2H, d, J=7.9 Hz, H^3 and H^5), 7.17 (1H, t, J=7.9 Hz, H^4), 0.76, 1.71, 1.94, 2.01 (12H, s, CH_3), 4.93, 5.26 (2H, s, CH); ^{13}C NMR ($CDCl_3$) δ=ca. 2.1 and 11.5 (complex, RhC and RhC′), pyridine ring 172.9 (d, $^1J_{PC}$=4.4 Hz, C^2), 122.2 (s, C^3), 135.2 (s, C^1), 116.5 (s, C^5), 171.5 (s, C^6), PPh_3 132.0 (d, $^1J_{PC}$=47.0 Hz, *i*-C), 134.8 (d, $^2J_{PC}$=8.8 Hz, *o*-C), 127.7 (br d, $^3J_{PC}$=8.8 Hz, *m*-C), 127.4 (d, $^3J_{PC}$=10.3 Hz, *m*-C′), 129.7 (s, *p*-C), 129.4 (s, *p*-C′), 26.8, 27.0, 28.9 (s, CH_3), 28.4 (d, $^3J_{PC}$=7.3 Hz, CH_3), 98.0, 98.7 (s, CH), 183.8, 186.7, 187.7 (s, C=O), 184.5 (br, C=O); ^{31}P NMR ($CDCl_3$) δ=34.0 (d, $^1J_{RhP}$=137 Hz, P_A), 37.3 (d, $^1J_{RhP}$=156 Hz, P_B). Found: C, 57.94; H, 4.92; N, 1.24%; Mol wt 1143. Calcd for $C_{53}H_{51}Cl_2NO_4P_2Rh_2$: C, 57.63; H, 4.65; N, 1.27%; M 1105.

Measurements. IR spectra were recorded in Nujol on a JASCO DS-701G spectrophotometer. ^{1}H and ^{13}C{^{1}H} NMR spectra were taken on a JEOL JNM GX-400 spectrometer at 400 and 100 MHz respectively using tetramethylsilane as internal reference. ^{31}P{^{1}H} NMR spectra were taken on JEOL JNM FX-60Q and 400-α instruments at 24.2 and 161.7 MHz, respectively, with H_3PO_4 used as an external reference. The FAB mass spectrum was obtained with a JEOL JMS AX-500 spectrometer in the positive-ion mode using 3-nitrobenzyl alcohol as a matrix, dichloromethane as a solvent and xenon as a bonbardment gas. The molecular weight was measured in dichloromethane at 27 °C with a vapor-pressure osmometry unit manufactured by Knauer, Berlin, Germany.

This work was partially supported by a Grant-in-Aid for Science Research No. 03453053 from the Ministry of Education, Science and Culture.

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