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Preliminary communication

SYNTHESIS AND BONDING OF STABLE, CATIONIC CARBONYL OR OLEFIN COMPLEXES OF Ni(II), Pd(II) AND Pt(II)

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SUMMARY

Thermally stable, cationic carbonyl or monoolefin complexes of Ni(II), Pd(II) and Pt(II), $[\eta^5\text{-}C_5H_5M(PR_3)L]ClO_4$ (M= Ni, Pd, Pt; PR_3= PPh_3, PPh_2Me, $PPhMe_2$; L= CO, C_2H_4, C_3H_6) have been prepared. Infrared and ^1H NMR spectroscopic studies of these complexes suggest the order of metal to ligand π-donation as Pt > Ni > Pd for the carbonyl and Pt > Pd for the ethylene complexes.

Systematic studies on the nature of metal-carbonyl and -olefin bonds in a series of complexes encompassing all of the nickel triad metals, especially in the formal oxidation state of two, have been few in number mainly because of the instabilities of Ni(II) and Pd(II) complexes with such ligands[1]. Puddephatt et al. recently deduced the extent of metal to ligand π-donation to decrease in the order Ni > Pt > Pd from examination of a rather wide range of reactivities of olefins toward the alkyl complexes of these metals[2]. Here we report a more direct comparison, on the basis of spectroscopic evidence, of the metal-carbonyl or -olefin

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bonds in complexes of type, $[\eta^5\text{-}C_5H_5M(PR_3)L]ClO_4$ (M= Ni, Pd, Pt; PR_3= PPh_3, PPh_2Me, $PPhMe_2$; L= CO, C_2H_4, C_3H_6), where the nickel and palladium analogs appear to represent the most stable cationic carbonyl or monoolefin complexes of these metals known.

Treatment of $\eta^5\text{-}C_5H_5M(PR_3)X$ (X= Cl, Br) with $AgClO_4$ in acetone under carbon monoxide or gaseous olefin at atmospheric pressure readily gave $[\eta^5\text{-}C_5H_5M(PR_3)L]ClO_4$* (M= Ni, Pd; see Table 1). The platinum analogs could be prepared from the reaction of $PtCl_2(PPh_3)L$ with C_5H_5Tl in methylene chloride followed by addition of $AgClO_4$. All the complexes thus prepared are fairly stable in the solid state at room temperature, but all the nickel complexes and <u>2c</u> gradually decomposed when dissolved in solvents such as methylene chloride and acetone at room temperature**. In Table 1 are shown the properties and infrared and ^1H NMR spectral data of the complexes.

The value of $\nu(CO)$ in the carbonyl complexes suggest the degree of metal to carbonyl π-donation to decrease in the order, Pt > Ni > Pd. It is also notable that the $\nu(CO)$ of <u>1a</u>, <u>1a'</u>, <u>1a"</u>, and <u>2a</u> are lower than those[3,4] of the four-coordinate, reportedly less stable carbonyl complexes of Ni(II) and Pd(II), respectively. This is most probably attributable to the strongly electron-donating ability of the penta-hapto C_5H_5 ligand, as confirmed also by comparison of $\nu(CO)$ of <u>3a</u> with that of $[\eta^3\text{-}C_3H_5Pt(PPh_3)CO]ClO_4$*** (2112 cm^{-1}).

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*CAUTION! Though we have experienced no troubles with the perchlorate salts prepared during the present study, special care must be taken in handling these in view of their potentially explosive nature.

**Satisfactory elemental analyses were obtained for the complexes shown in Table 1 except for <u>1a'</u>, <u>1a"</u> and <u>1b</u> which were characterized by spectral data.

***This was prepared from $\eta^3\text{-}C_3H_5Pt(PPh_3)Cl$ and $AgClO_4$ under CO.

Table 1. Properties and Spectral Data[a] of $[\eta^5\text{-}C_5H_5M(PR_3)L]ClO_4$

Complex	M	PR$_3$	L	Color	m.p.[b] (°C)	ν(CO) (cm^{-1})	$\delta(C_5H_5)$[c] (ppm)	$\delta(C_2H_4)$ (ppm)	$\Delta\delta$[d] (ppm)
1a	Ni	PPh$_3$	CO	green	144	2093	5.72(s)		
1a'	Ni	PPh$_2$Me	CO	brown	e	2090	5.78(s)		
1a''	Ni	PPhMe$_2$	CO	brown	e	2086	5.79(s)		
1b	Ni	PPhMe$_2$	C_2H_4	red	e		5.13(s)	3.61(br)	1.75
2a	Pd	PPh$_3$	CO	violet	167	2113	5.99(d)		
2b	Pd	PPh$_3$	C_2H_4	violet	156		5.98(d)	4.03(d)[f]	1.33
2c	Pd	PPh$_3$	C_3H_6	violet	145		5.83(d)	g	
3a	Pt	PPh$_3$	CO	orange	195	2081	5.96(d)		
3b	Pt	PPh$_3$	C_2H_4	orange	170		5.95(d)	2.97(br)[h]	2.39

[a] IR in methylene chloride, ^{1}H NMR in $CDCl_3$ at room temperature. s= singlet, d= doublet, br= broad, m= multiplet. [b] With decomposition.

[c] Couplings with ^{31}P (2.0- 2.5 Hz) were observed in **2** and **3**.

[d] $\Delta\delta = \delta(\text{free } C_2H_4) - \delta(C_2H_4 \text{ in complex})$. [e] Not measured.

[f] J_P= 2.5 Hz. [g] $\delta(=CH_2)$ 4.20(m) and 4.52(m), $\delta(=CH-)$ 5.50(m).

[h] J_{Pt}= 70 Hz.

The ethylene proton resonances in **1b**, **2b** and **3b** were observed as magnetically equivalent at room temperature (Table 1), indicating that rotation of ethylene about the metal-ethylene bond axis is rapid on the NMR time scale at room temperature [*]. These resonances of **2b** in methylene chloride only became broader on cooling down to -90°C, while those of **3b** split into apparent AA'MM'X multiplets at -60°C (δ 3.75, 2H, J_H= 13 Hz, $J_{H'}$= 6 Hz, J_{Pt}=

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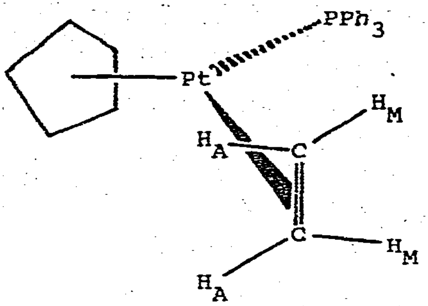
[*] Addition of excess ethylene to the solution of each ethylene complex at room temperature caused no change in the chemical shifts and the shape of the coordinated ethylene proton resonances, suggesting that intermolecular exchange of ethylene is slow on the NMR time scale.

76 Hz; δ 2.02, 2H, J_P= 4.4 Hz, J_{Pt}= 64 Hz) (coalescence temperature ca. 0°C). This pattern is predicted for the ethylene protons and the phosphorus nucleus in the configuration shown below, where the rotation of ethylene is slow at -60°C. Further, the value of the



upfield shift for the ethylene proton resonances on coordination, $\Delta\delta$ is larger in 3b than in 2b. These facts are best interpreted in terms of more effective metal-ethylene π-interaction in the platinum than in the palladium complex[*]. However, we cannot determine the relative order of the π-interaction in 1b and 2b or 3b at the moment.

The ligands L in 1~3 could readily be replaced by some bases such as PR_3 and pyridine. The reaction of 2b or 3b with CO similarly afforded 2a or 3a, respectively. Notably, passing ethylene gas at atmospheric pressure through an acetone solution of 2a for about 30 min at room temperature resulted in complete formation of 2b. Conversion of the metal carbonyl to the π-ethylene complex under such mild conditions seems very unusual, and certainly warrants further investigation. Similar treatments of 1a and 3a with ethylene resulted merely in recovery of these complexes. Other reactions of 1~3, including nucleophilic addition to the coordinated ligands, are being studied.

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[*] In view of the covalent radii of the metal atoms, the extent of steric hindrance with regard to the rotation of ethylene may possibly be about equal in 2b and 3b.

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