

## COMPARISON OF ORGANO-NICKEL(II), -PALLADIUM(II) AND -PLATINUM(II) COMPLEXES

### II \*. PREPARATION AND ACIDITIES OF CATIONIC CYCLIC ALKYL(ALKOXY)CARBENE COMPLEXES

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(Received September 8th, 1980)

#### Summary

Five- and six-membered  $\alpha$ -alkoxyvinylmetal(II) complexes of type *trans*- $C_6Cl_5M(PPhMe_2)_2\bar{C}=\overline{CH(CH_2)_nO}$  (abbr.  $[M]-\bar{C}=\overline{CH(CH_2)_nO}$ , where  $M = Ni, Pd, Pt$ ;  $n = 2$  and  $3$ ), were prepared by the reaction of  $[M]-Cl$  and  $Li-\bar{C}=\overline{CH(CH_2)_nO}$ , and were treated with perchloric acid to give cationic five- and six-membered cyclic alkyl(alkoxy)carbene complexes,  $[M]-^+\bar{C}CH_2(CH_2)_nOClO_4^-$ . The relative Brønsted acidity of  $[M]-^+\bar{C}CH_2(CH_2)_nO$  followed the order  $M = Ni < Pd > Pt$  and  $[M]-^+\bar{C}CH_2CH_2CH_2O < [M]-^+C(OMe)Me < [M]-^+\bar{C}CH_2CH_2CH_2CH_2O$ .

#### Introduction

Recently, we have prepared and compared the properties of a series of  $\alpha$ -methoxyvinylmetal(II) complexes of type *trans*- $C_6Cl_5M(PPhMe_2)_2C(OMe)=CH_2$ , and the corresponding cationic methyl(methoxy) carbene complexes, *trans*- $[C_6Cl_5M(PPhMe_2)_2\{C(OMe)Me\}]^+$ , where  $M = Ni^{II}, Pd^{II}$  and  $Pt^{II}$  [1]. These two types of complexes are related to each other by facile and reversible protonation, and, at the same time, these carbon ligands are representative of the lowest and the highest  $\pi$ -accepting carbon ligands, respectively [2,3]. In this report [1], we compared the relative Brønsted acidities of these carbene complexes, and discussed the M–C bonding properties of these two series of complexes based on spectral data. The present paper is concerned with analogous work on two systems which have a cyclic carbon ligand coordinated to the cationic *trans*- $C_6Cl_5M(PPhMe_2)_2$  moieties (abbr.  $[M]-$ , where  $M = Ni, Pd, Pt$ ). In these cyclic carbon ligand systems there is a greater stereochemical resem-

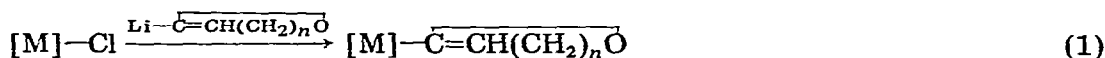
\* For part I see ref. 1.

blance between the vinyl and the carbene complexes than in the previous system. In the latter, the carbene ligand had no rotational freedom about the M—C(carbene) and the C(carbene)—O bonds, while the corresponding bonds of vinyl complexes had rotational freedom.

## Results and discussion

### Preparation of complexes

In analogy with methyl vinyl ether [1], 2,3-dihydrofuran was lithiated with *n*-butyllithium in tetrahydrofuran. Treatment of the lithium reagent with [M]—Cl afforded the expected dihydrofuryl complexes, [M]— $\overline{\text{C}}=\text{CHCH}_2\text{CH}_2\text{O}$  (eq. 1; *n* = 2). Using 2,3-dihydropyran in place of 2,3-dihydrofuran, the dihydropyranyl complexes, [M]— $\overline{\text{C}}=\text{CHCH}_2\text{CH}_2\text{CH}_2\text{O}$ , also could be obtained (eq. 1; *n* = 3).



[M]— = *trans*-C<sub>6</sub>Cl<sub>5</sub>M(PPhMe<sub>2</sub>)<sub>2</sub>— (M = Ni, Pd, Pt); *n* = 2 and 3.

When ethereal solutions of these vinyl complexes were treated with 60% aqueous perchloric acid, the corresponding cationic cyclic alkyl(alkoxy)carbene complexes, [M]— $\overline{\text{C}}\text{CH}_2(\text{CH}_2)_n\text{OClO}_4^-$ , precipitated and were isolated in good yield (eq. 2). [Ni]— $\overline{\text{C}}\text{CH}_2\text{CH}_2\text{CH}_2\text{OClO}_4^-$  had been prepared previously by the reaction of [Ni]—C≡CCH<sub>2</sub>CH<sub>2</sub>OH and aqueous perchloric acid [2], but analogous treatment of [Pd]—C≡CCH<sub>2</sub>CH<sub>2</sub>OH resulted in the cleavage of the Pd—C bond [1]. In contrast to the five-membered cyclic alkyl(alkoxy)carbene complexes, six-membered cyclic carbene complexes are quite uncommon. *trans*-[(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Mo(CO)<sub>2</sub>(PPh<sub>3</sub>)( $\overline{\text{C}}\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$ )]<sup>+</sup> [4] and *cis*-Mn(CO)<sub>4</sub>(I)-( $\overline{\text{C}}\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$ ) [5] have been prepared by intramolecular cyclization of ω-haloacylmethyl intermediates.

As was found for [M]— $\overline{\text{C}}(\text{OMe})\text{Me}$  complexes [1,2], treatment of [M]— $\overline{\text{C}}\text{CH}_2(\text{CH}_2)_n\text{O}$  complexes with triethylamine resulted in the recovery of [M]— $\overline{\text{C}}=\text{CH}(\text{CH}_2)_n\text{O}$  complexes (eq. 2). The C(carbene)—CH<sub>2</sub> resonance in the <sup>1</sup>H NMR spectra of [M]— $\overline{\text{C}}\text{CH}_2(\text{CH}_2)_n\text{O}$  complexes in dichloromethane solution readily disappeared on addition of an excess of CH<sub>3</sub>OD due to H—D exchange. The vinyl complexes also showed analogous H—D exchange of the vinyl proton.

### Brønsted acidities of cationic cyclic alkyl(alkoxy)carbene complexes

The relative acidities of [M]— $\overline{\text{C}}\text{CH}_2(\text{CH}_2)_n\text{O}$  complexes (eq. 3) were determined essentially by the same procedure [1] \* using <sup>1</sup>H NMR spectroscopy. The results are summarized in Table 1, which also includes the data reported

\* Closely related work has been reported by Casey et al. for (CO)<sub>5</sub>Cr{C(OMe)Me} [6] and (CO)<sub>5</sub>Cr( $\overline{\text{C}}\text{CHRCH}_2\text{CH}_2\text{O}$ ) [7], which are as acidic as *p*-cyanophenol (pK<sub>a</sub> = 8).

TABLE 1

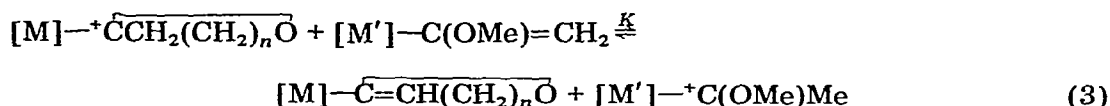
RELATIVE BRØNSTED ACIDITIES <sup>a</sup> OF THE CATIONIC ALKYL(ALKOXY)CARBENE COMPLEXES  $\text{trans-}[C_6Cl_5M(PPhMe_2)_2\{C(OR')R\}]ClO_4$ .

C(OR')R	M =	Ni	Pd	Pt
C(OMe)Me		1.0 <sup>b</sup>	13.2 <sup>c</sup>	0.94 <sup>c</sup>
$\overline{C}CH_2CH_2CH_2\overline{O}$		0.15	1.1	0.18
$\overline{C}CH_2CH_2CH_2CH_2\overline{O}$		19	330	14

<sup>a</sup> Represented in the equilibrium constant of the reaction shown in eq. 4 in  $CD_2Cl_2$ . <sup>b</sup> This complex has about the same  $pK_a$  as the conjugate acids of triethanol amine or 2,4,6-trimethylpyridine [2].

<sup>c</sup> These data have been reported previously [1].

previously for the  $[M]^{-+}C(OMe)Me$  complexes [1].



As is seen from Table 1, the metal dependence of the acidities is quite similar among these three series of carbene complexes, palladium complexes showing the highest acidity, and nickel and platinum complexes being comparable in acidity. The carbene dependence of the acidity is in the order of  $\overline{C}CH_2CH_2CH_2\overline{O} < C(OMe)Me < \overline{C}CH_2CH_2CH_2CH_2\overline{O}$  for all the three metal series. The lowest acidity of  $[M]^{-+}\overline{C}CH_2CH_2CH_2\overline{O}$  seems to be correlated to the high stability of organic compounds of type,  $R^{-+}\overline{C}CH_2CH_2CH_2\overline{O}$  [8].

#### IR and NMR spectra

The IR and <sup>1</sup>H NMR spectral data are shown in Table 2.  $[M]^{-}\overline{C}=\overline{C}H(CH_2)_n\overline{O}$  complexes displayed in the IR spectra a characteristic  $\nu(C=C)$  band. The frequency increased in the same order, Ni < Pd < Pt, as was found for M-C(OMe)=CH<sub>2</sub> complexes [1]. An analogous progressive increase was observed for the  $\nu(C-O)$  band. The O-CH<sub>2</sub> proton and the P-CH<sub>3</sub> proton resonances in the <sup>1</sup>H NMR spectra of  $[M]^{-}\overline{C}=\overline{C}H(CH_2)_n\overline{O}$  complexes are magnetically shielded in the order of Ni > Pd > Pt. In such ways we again observed no peculiarity of palladium in the spectral data of  $[M]^{-}\overline{C}=\overline{C}H(CH_2)_n\overline{O}$  complexes, and these data are in accord with the fact that the M-C bond is polarized in the order of Ni > Pd > Pt, which parallels the relative electronegativities of these +2 metal ions [9] and explains the lower acidity of nickel complexes vs. those of palladium.

The P-CH<sub>3</sub> protons of  $[M]^{-+}\overline{C}CH_2(CH_2)_n\overline{O}$  complexes also are magnetically shielded in the order Ni > Pd > Pt, while a reverse order of shielding effect by the metal was observed for the C(carbene)-CH<sub>2</sub> proton resonance of  $[M]^{-+}\overline{C}CH_2CH_2CH_2\overline{O}$ , and an order of Ni < Pd > Pt was observed for most of the other carbene protons in  $[M]^{-+}\overline{C}CH_2(CH_2)_n\overline{O}$  series. The pronounced shielding effect by platinum is in agreement with our previous results for  $[M]^{-+}C(OMe)Me$  complexes [1], due to extensive  $d_{\pi}-p_{\pi}$  back bonding from the metal to the carbene carbon atom.

TABLE 2

IR ( $\text{cm}^{-1}$ )<sup>a</sup> AND <sup>1</sup>H NMR (ppm)<sup>b</sup> SPECTRAL DATA FOR  $[\text{M}]-\overline{\text{C}}=\text{CH}(\text{CH}_2)_n\text{O}$  (I) AND  $[\text{M}]-\overline{\text{C}}\text{CH}_2(\text{CH}_2)_n\text{OClO}_4^-$  (II) ( $[\text{M}]- = \text{trans-C}_6\text{Cl}_5\text{M}(\text{PPhMe}_2)_2-$ )<sup>c</sup>

Complex	n	Assignment	M = Ni	Pd	Pt
I	2	$\nu(\text{C}=\text{C})$	1550s (1561m)	1565s (1569m)	1570s (1573m)
		$\nu(\text{COC})$	1005s (1007s)	1008s (1012s)	1010s (1018s)
		$\delta(\text{P}-\text{CH}_3)$	1.45t [7.5]	1.51t [7.1]	1.64tt [34.4][7.1]
		$\delta(\text{C}=\text{CH})$	4.26qn [2.5][2.5]	4.28qn [2.0][2.0]	4.20m [2.4]
		$\delta(\text{CH}_2\text{CH}_2\text{O})$	2.22m	2.28m	2.28m
		$\delta(\text{CH}_2\text{O})$	3.64t [9.1]	3.86t [9.4]	3.88t [9.1]
I	3	$\nu(\text{C}=\text{C})$	1586s (1584s)	1596s (1592s)	1600s (1594s)
		$\nu(\text{COC})$	1043s (1035s)	1040s (1036s)	1040s (1040s)
		$\delta(\text{P}-\text{CH}_3)$	1.49t [7.5]	1.55t [6.9]	1.65tt [35.2][7.4]
		$\delta(\text{C}=\text{CH})$	4.07m	4.07m	4.07br
		$\delta(\text{CH}_2\text{O})$	3.41t [5.2]	3.60t [5.2]	3.65t [5.0]
		$\delta(\text{CH}_2\text{CH}_2\text{O})$ <sup>d</sup>	1.78m	1.75m	overlapped
II	2	$\delta(\text{P}-\text{CH}_3)$	1.56t [8.4]	1.59t [7.9]	1.70tt [34.5][8.6]
		$\delta(^+\text{CCH}_2)$	2.88t [7.9]	2.72t [8.1]	2.34t [7.7]
		$\delta(\text{CH}_2\text{CH}_2\text{O})$	1.14qn [7.9]	1.33qn [8.1]	1.33qn [7.7]
		$\delta(\text{CH}_2\text{O})$	4.64tt [7.9][1.0]	4.83t [8.1]	4.70tt [8.4][7.7]
II	3	$\delta(\text{P}-\text{CH}_3)$	1.54br	1.57t [7.8]	1.68tt [33.9][8.0]
		$\delta(^+\text{CCH}_2)$	2.60m	2.64m	2.25m
		$\delta(\text{CH}_2\text{O})$	4.38br	4.48br	4.37br
		$\delta(\text{CH}_2\text{CH}_2\text{O})$	1.19 qn [6.5]	1.28qn [6.4]	1.24qn [6.5]
		$\delta(\text{CH}_2\text{CH}_2\text{CH}_2\text{O})$	0.71qn [6.5]	0.88qn [6.4]	0.88qn [6.5]

<sup>a</sup> In Nujol mull. The dichloromethane solution data are shown in parentheses. <sup>b</sup> In dichloromethane. The coupling constants,  $J(\text{P})$ ,  $J(\text{H})$  and  $J(\text{Pt})$ , are shown in brackets in Hz. <sup>c</sup> Some data for nickel complexes have been reported in ref. 2. <sup>d</sup> The other  $\text{CH}_2$  resonances were obscured by  $\text{P}-\text{CH}_3$  resonance.

The <sup>1</sup>H NMR spectrum in the  $\text{P}-\text{CH}_3$  proton resonance region of  $[\text{Ni}]-\overline{\text{C}}=\text{CHCH}_2\text{CH}_2\text{CH}_2\text{O}$  is temperature-dependent, exhibiting a doublet with shoulders on both sides at low temperatures. The observation can be explained in terms of hindered rotation about the  $\text{Ni}-\text{C}$  bond, which generates diastereomeric methyl groups on the phosphine ligand. The coalescence temperature was  $-39^\circ\text{C}$ , and the rotational barrier ( $\Delta G_{234}^\ddagger$ ) was calculated to be 11.8 kcal/mol. In the spectra of the palladium and platinum complexes, we observed no clear evidence for such hindered rotation down to  $-80^\circ\text{C}$ , probably due to their larger covalent radii. An analogous temperature dependence of the <sup>1</sup>H NMR spectrum has been reported for the  $[\text{Ni}]-\overline{\text{C}}\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$  complex [2]. The spectrum of  $[\text{Ni}]-\overline{\text{C}}\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$  is also temperature dependent with a coalescence temperature of  $15^\circ\text{C}$ , from which a rotational barrier ( $\Delta G_{288}^\ddagger$ ) of 14.4 kcal/mol could be calculated.

The <sup>13</sup>C {H} NMR spectral data of relevant carbons for  $[\text{M}]-\overline{\text{C}}=\text{CHCH}_2\text{CH}_2\text{O}$  and  $[\text{M}]-\overline{\text{C}}\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$  complexes are summarized in Table 3. The resonances were assigned as described previously [1]. The data in the Table reveal that the shieldings of  $\text{M}-\text{C}$  carbon nuclei decrease greatly upon going from the  $[\text{M}]-\overline{\text{C}}=\text{CHCH}_2\text{CH}_2\text{O}$  to the  $[\text{M}]-\overline{\text{C}}\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$  complexes in apparent agreement

TABLE 3

THE RELEVANT  $^{13}\text{C}\{^1\text{H}\}$  NMR SPECTRAL DATA (ppm) <sup>a</sup> FOR  $[\text{M}]-\overline{\text{C}}=\text{CHCH}_2\text{CH}_2\text{O}$  AND  $[\text{M}]^{-+}\overline{\text{C}}\text{CH}_2\text{CH}_2\text{CH}_2\text{OClO}_4^-$  ( $[\text{M}]^- = \text{trans-}C_6Cl_5M(\text{PPhMe}_2)_2^-$ ) IN  $\text{CD}_2\text{Cl}_2$

Complexes	Assignments	M = Ni	Pd	Pt
$[\text{M}]-\overline{\text{C}}=\text{CHCH}_2\text{CH}_2\text{O}$	$\delta(\text{M}-\text{C})$	174.2t [48.7]	171.9t [24.9]	164.9t [20.6]
	$\delta(\text{C}=\text{CH})$	105.7t [8.8]	103.2t [12.5]	102.6tt [92.7][8.1]
	$\delta(\text{O}-\text{CH}_2)$	68.5s	68.8s	68.5t [47.1]
	$\delta(\text{CH}_2\text{CH}_2\text{O})$	31.3s	30.9s	31.5t [35.3]
	$\delta(\text{P}-\text{CH}_3)$	13.3t [29.4]	13.9t [30.1]	13.43tt [44.1][37.5]
$[\text{M}]^{-+}\overline{\text{C}}\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$	$\delta(\text{M}^{-+}\text{C})$	322.6t [45.6]	316.4t [20.6]	295.6t [17.6]
	$\delta(\text{M}^{-+}\text{C}-\text{CH}_2)$	55.0s	57.0s	57.5s
	$\delta(\text{O}-\text{CH}_2)$	91.0s	92.1s	90.2t [57.4]
	$\delta(\text{CH}_2\text{CH}_2\text{O})$	19.4s	19.1s	19.7t [17.6]
	$\delta(\text{P}-\text{CH}_3)$	12.7t [32.4]	13.3t [32.4]	13.1tt [39.7][39.7]
	$\Delta\delta(\text{M}-\text{C})$	148.4	144.5	130.7
	$\Delta\delta(\text{M}-\text{C}-\text{C})$	-51.4	-48.2	-46.8
	$\Delta\delta(\text{O}-\text{CH}_2)$	22.5	23.3	21.7
	$\Delta\delta(\text{CH}_2\text{CH}_2\text{O})$	-11.9	-11.8	-11.8
	$\Delta\delta(\text{P}-\text{CH}_3)$	-0.6	-0.6	-0.3

<sup>a</sup> The coupling constants,  $J(\text{P})$  and  $J(\text{Pt})$ , are shown in parentheses in Hz.

with the high concentration of positive charge on the carbon atom. The shielding difference values,  $\Delta\delta$ , which also are shown in the Table, decrease in the order of  $\text{Ni} \geq \text{Pd} > \text{Pt}$ . These results are similar to those observed for  $[\text{M}]-\text{C}(\text{OMe})=\text{CH}_2$  and  $[\text{M}]^{-+}\text{C}(\text{OMe})\text{Me}$  system [1], and the discussion described there may also hold here.

## Experimental

Infrared spectra,  $^1\text{H}$  NMR spectra and  $^{13}\text{C}$  NMR spectra were recorded as described previously [1]. The starting complexes,  $\text{trans-}C_6Cl_5M(\text{PPhMe}_2)_2\text{Cl}$  ( $M = \text{Ni}$  [2],  $\text{Pd}$  [1],  $\text{Pt}$  [1]) were prepared as described previously. Melting points and analytical data for new complexes are summarized in Table 4.

### $\text{trans-}C_6Cl_5\text{Ni}(\text{PPhMe}_2)_2\overline{\text{C}}=\text{CHCH}_2\text{CH}_2\text{O}$

Lithiation of 2,3-dihydrofuran was performed in a round-bottomed 100-ml flask fitted with magnetic stirring bar under a nitrogen atmosphere. To a solution of 2,3-dihydrofuran (2 ml, 26.4 mmol) in 40 ml of dry THF was added a 15% n-hexane solution of n-butyllithium (12.4 ml, 20 mmol) at  $0^\circ\text{C}$ , and the mixture was stirred at room temperature for 2 h. A solution of  $\text{trans-}C_6Cl_5\text{Ni}(\text{PPhMe}_2)_2\text{Cl}$  (2.48 g, 4 mmol) in 20 ml of dry THF was added at  $-20^\circ\text{C}$ . The mixture was allowed to warm to room temperature over a 1 h period, and was kept stirring for 1 h. Cold water containing ammonium chloride was added, and most of organic solvents were removed under reduced pressure. The precipitate in the water phase was extracted with diethyl ether. The ether layer was separated, the solvent was evaporated, and the residue was recrystallized from acetone/methanol to give yellow crystals of  $\text{trans-}C_6Cl_5\text{Ni}(\text{PPhMe}_2)_2\overline{\text{C}}=\text{CHCH}_2\text{CH}_2\text{O}$  (0.685 g, 26%). This complex was identical with that reported previously [2].

TABLE 4

ANALYTICAL DATA FOR THE NEW ORGANO-NICKEL(II), -PALLADIUM(II) AND -PLATINUM(II) COMPLEXES [M]-R AND [M]-<sup>+</sup>LCIO<sub>4</sub><sup>-</sup> ([M]- = *trans*-C<sub>6</sub>Cl<sub>5</sub>M(PPhMe<sub>2</sub>)<sub>2</sub>-)

Complex		M.p. (°C)	Analyses (found (calcd.) (%))		
M	R or L		C	H	Cl
Ni	$\overline{\text{C}=\text{CHCH}_2\text{CH}_2\text{CH}_2\text{O}}$	136-137 <sup>a</sup>	48.13 (48.59)	4.36 (4.38)	26.91 (26.56)
Ni	$\overline{\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}}$	139-140 <sup>a</sup>	42.04 (42.23)	4.19 (3.94)	27.40 (27.70)
Pd	$\overline{\text{C}=\text{CHCH}_2\text{CH}_2\text{O}}$	116 <sup>a</sup>	44.59 (44.54)	4.05 (3.88)	25.43 (25.28)
Pd	$\overline{\text{CCH}_2\text{CH}_2\text{CH}_2\text{O}}$	153 <sup>a</sup>	38.79 (38.96)	3.73 (3.52)	26.68 (26.54)
Pd	$\overline{\text{C}=\text{CHCH}_2\text{CH}_2\text{CH}_2\text{O}}$	135-136 <sup>a</sup>	45.05 (45.35)	4.10 (4.09)	25.29 (24.79)
Pd	$\overline{\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}}$	137-139 <sup>a</sup>	40.20 (39.76)	3.95 (3.71)	25.73 (26.08)
Pt	$\overline{\text{C}=\text{CHCH}_2\text{CH}_2\text{O}}$	148-149 <sup>a</sup>	39.65 (39.54)	3.48 (3.45)	22.45 (22.44)
Pt	$\overline{\text{CCH}_2\text{CH}_2\text{CH}_2\text{O}}$	197-198	35.06 (35.08)	3.13 (3.17)	24.13 (23.90)
Pt	$\overline{\text{C}=\text{CHCH}_2\text{CH}_2\text{CH}_2\text{O}}$	145-147	40.60 (40.34)	3.71 (3.64)	21.90 (22.05)
Pt	$\overline{\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}}$	169-171 <sup>a</sup>	36.28 (35.86)	3.62 (3.34)	

<sup>a</sup> Decomposed.*trans*-C<sub>6</sub>Cl<sub>5</sub>Pd(PPhMe<sub>2</sub>)<sub>2</sub> $\overline{\text{C}=\text{CHCH}_2\text{CH}_2\text{O}}$ 

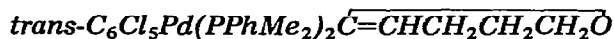
In a similar manner as above, this complex was prepared from *trans*-C<sub>6</sub>Cl<sub>5</sub>Pd-(PPhMe<sub>2</sub>)<sub>2</sub>Cl (2.0 g, 3 mmol) in 61% yield. The crystals became gray in color in several months even at ca. 0°C.

*trans*-C<sub>6</sub>Cl<sub>5</sub>Pt(PPhMe<sub>2</sub>)<sub>2</sub> $\overline{\text{C}=\text{CHCH}_2\text{CH}_2\text{O}}$ 

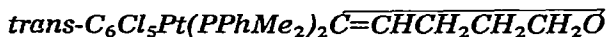
In a similar manner as above, this complex was prepared from *trans*-C<sub>6</sub>Cl<sub>5</sub>Pt-(PPhMe<sub>2</sub>)<sub>2</sub>Cl (2.3 g, 3 mmol) in 46% yield.

*trans*-C<sub>6</sub>Cl<sub>5</sub>Ni(PPhMe<sub>2</sub>)<sub>2</sub> $\overline{\text{C}=\text{CHCH}_2\text{CH}_2\text{CH}_2\text{O}}$ 

To a solution of 2,3-dihydropyran (1 ml, 11 mmol) in 20 ml of dry THF was added a 15% n-hexane solution of n-butyllithium (6.2 ml, 10 mmol) at 0°C under a nitrogen atmosphere. The mixture was stirred at room temperature for 1 h, and then *trans*-C<sub>6</sub>Cl<sub>5</sub>Ni(PPhMe<sub>2</sub>)<sub>2</sub>Cl (1.24 g, 2 mmol) dissolved in 10 ml of dry benzene was added at 0°C. The mixture was stirred for 1 h at 0°C, and then for an additional 1 h at room temperature. Cold water containing ammonium chloride was added, and most of the organic solvents were removed under reduced pressure. The aqueous phase which contained a precipitate was extracted with diethyl ether. The ether layer was separated, the solvent was evaporated, and the residue was recrystallized from acetone/methanol to give yellow crystals of *trans*-C<sub>6</sub>Cl<sub>5</sub>Ni(PPhMe<sub>2</sub>)<sub>2</sub> $\overline{\text{C}=\text{CHCH}_2\text{CH}_2\text{CH}_2\text{O}}$  (0.702 g, 53%).



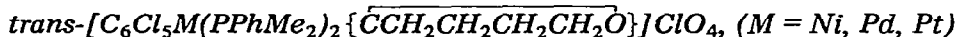
In a similar manner as above, this complex was prepared from *trans*-C<sub>6</sub>Cl<sub>5</sub>Pd-(PPhMe<sub>2</sub>)<sub>2</sub>Cl (1.0 g, 1.5 mmol) in 71% yield. The crystals also became gray in color in several months at ca. 0°C.



In a similar manner as above, this complex was prepared from *trans*-C<sub>6</sub>Cl<sub>5</sub>Pt-(PPhMe<sub>2</sub>)<sub>2</sub>Cl (1.5 g, 2 mmol) in 29% yield.



To a solution of *trans*-C<sub>6</sub>Cl<sub>5</sub>M(PPhMe<sub>2</sub>)<sub>2</sub> $\overline{\text{C}=\text{CHCH}_2\text{CH}_2\text{O}}$  (0.2–1.0 mmol) in diethyl ether (10–30 ml) was added dropwise 60% aqueous perchloric acid (a slight excess). The precipitate which resulted was recrystallized from dichloromethane/n-hexane or from ethanol to give crystals of *trans*-[C<sub>6</sub>Cl<sub>5</sub>M-(PPhMe<sub>2</sub>)<sub>2</sub>{ $\overline{\text{CCH}_2\text{CH}_2\text{CH}_2\text{O}}$ }]ClO<sub>4</sub> in yields of 86% (Ni), 84% (Pd) and 78% (Pt). The nickel complex was identical with that reported previously [2].



These complexes were prepared in 61% (Ni), 58% (Pd) and 67% (Pt) yields in similar manner as above using *trans*-C<sub>6</sub>Cl<sub>5</sub>M(PPhMe<sub>2</sub>)<sub>2</sub> $\overline{\text{C}=\text{CHCH}_2\text{CH}_2\text{CH}_2\text{O}}$ . They were recrystallized from ethanol.

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