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

I. PREPARATION AND ACIDITIES OF CATIONIC METHYL(METHOXY)CARBENE COMPLEXES

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Summary

α-Methoxyvinylmetal(II) complexes of the type *trans*-$C_6Cl_5M(PPhMe_2)_2C(OMe){=}CH_2$ (abbr. [M]—$C(OMe){=}CH_2$, where M = Ni, Pd, Pt) were prepared by the reaction of [M]—Cl and Li—$C(OMe){=}CH_2$, and were treated with perchloric acid to give cationic methyl(methoxy)carbene complexes, [M]—$^+C(OMe)Me$, ClO_4^-. Ethynylmetal(II) complexes, [M]—C≡CH, were prepared by the reaction of [M]—Cl, silver perchlorate and HC≡CH in the presence of triethylamine, and were treated with perchloric acid in the presence of methanol to give either [M]—$^+C(OMe)Me, ClO_4^-$ (M = Ni, Pt) or $[Pd]^+$—OH_2, ClO_4^-. The relative Brønsted acidity of [M]—$^+C(OMe)Me$ was found to be in the order M = Ni < Pd > Pt. From the IR, ^1H NMR and ^{13}C NMR spectral investigations, the order was explained in terms of the largest σ-bonding polarity for Ni in the M—C bond of [M]—$C(OMe){=}CH_2$ and the largest back π-donor ability for Pt in the M—C bond of [M]—$^+C(OMe)Me$.

Introduction

Well-characterized organo(alkoxy)carbene complexes are now known for many transition metals [1—4], and we have recently reported the preparation and properties of some organonickel(II) carbene complexes of type *trans*-$[C_6Cl_5Ni(PPhMe_2)_2\{C(OR')R\}]ClO_4$, where R = alkyl [5] or aryl [6]. One of the characteristic properties of these nickel(II) carbene complexes is the facile and reversible deprotonation of the methyl(alkoxy)carbene ligands to give α-alkoxyvinylnickel(II) complexes, *trans*-$C_6Cl_5Ni(PPhMe_2)_2C(OR'){=}CH_2$ (eq. 1) [5]. Secondly, as the electronic spectral investigation revealed, the carbene ligands are situated at the highest position (λ_{max} = 322 ~ 335 nm) in the spectrochemical series of carbon ligands, while the α-alkoxyvinyl groups are the lowest position (λ_{max} = 373 ~ 385 nm) [5–8].

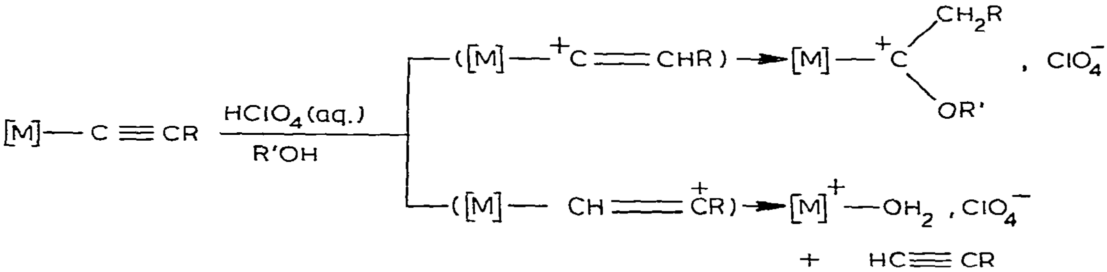
No such carbene complex of palladium(II) is known, although a variety of analogous platinum(II) carbene complexes have been reported [9–12]. When such a palladium complex is obtained, it will provide us an opportunity for a detailed comparison of these metal chemistries. The present study is concerned with our attempts to prepare a series of alkyl(alkoxy)carbene complexes of the cationic *trans*-$C_6Cl_5M(PPhMe_2)_2$-moieties (abbr. [M]—, where M = Ni, Pd, Pt). It also is concerned with a comparison of their relative acidities (eq. 1).

(1)

[M]— = *trans* — $C_6Cl_5M(PPhMe_2)_2$ — ; M = Ni, Pd, Pt.

Results and discussion

The cationic nickel(II) methyl(alkoxy)carbene complexes, [Ni]—$^+$C(OR')Me, were prepared by the addition of perchloric acid to a solution of [Ni]—C≡CH in the presence of alcohols (eq. 2), although different behavior, e.g., eq. 3, has been observed with some other [Ni]-C≡CR complexes [5]. Such a reaction to give platinum(II) carbene complexes also is known for a variety of alkynylplatinum(II) complexes [10]. Consequently, this method was first applied to [Pd]—C≡CR and [Pt]—C≡CR complexes in the present study.



(2)

(3)

Preparation and reactions of alkynylmetal(II) complexes

A reaction of [Ni]—Cl with silver perchlorate, followed by treatment with a terminal alkyne in the presence of a base has been found to be a convenient method for the preparation of a series of [Ni]—C≡CR complexes [5,13]. This method could be used successfully in the present study for the preparation of a series of [Pd]—C≡CR (R = H, Me, Ph, CH_2CH_2OH) and [Pt]—C≡CR (R = H, Ph) complexes. A method developed recently by Sonogashira et al. [14–16] also could be used to prepare some of these [M]—C≡CR complexes.

When the [Pd]—C≡CH complex was treated with aqueous perchloric acid in the presence of alcohols, a cleavage of the Pd—C bond resulted, giving the $[Pd]^+$—OH_2 complex (eq. 3). Analogous Pd—C bond cleavages were observed for all the other [Pd]—C≡CR complexes, and no palladium(II) carbene complex could be obtained by this method. When the platinum complex, [Pt]—C≡CH, was treated with perchloric acid in the presence of methanol, the expected carbene complex, [Pt]—$^+$C(OMe)Me, could be obtained in a good yield. The complex, [Pt]—C≡CPh, also afforded the carbene complex, [Pt]—$^+$C(OMe)CH$_2$Ph, although [Ni]—C≡CPh did not react [5].

Chisholm et al. [10] and we [5] have proposed a cationic vinylidene complex, M—C$^+$=CHR, as the reactive intermediate in the formation of alkoxycarbene complexes from alkynylmetals, M—C≡CR. Recent publications have described the isolation and characterization of such complexes of manganese [17,18], rhenium [19], iron [20] and ruthenium [21]. On the other hand, it is also probable that a protonation of alkynylmetals can occur on the α-carbon to give a M—CH=CR$^+$ intermediate which would result in the cleavage of the M—C bond. In fact, we reported such a case for the reaction of [Ni]—C≡CMe [5].

Preparation and protonation of α-methoxyvinylmetal(II) complexes

The finding of facile and reversible deprotonation of the carbene ligand in [Ni]—$^+$C(OR')Me complexes to give α-alkoxyvinylnickel complexes, [Ni]—C(OR')=CH$_2$ (eq. 1), suggests a new and more direct method of preparation of cationic alkyl(alkoxy)carbene complexes if the appropriate α-alkoxyvinylmetal can be prepared by any other method.

Baldwin and co-workers have prepared α-methoxyvinyllithium by a reaction of methyl vinyl ether and tert-butyllithium in dry tetrahydrofuran at −65°C [22]. We prepared this reagent in an analogous manner but using n-butyllithium at −50—0°C. Metathetic reaction of [Pd]—Cl with the lithium reagent afforded the expected [Pd]—C(OMe)=CH$_2$ complex in a good yield (eq. 4). Both [Ni]—C(OMe)=CH$_2$ [5] and [Pt]—C(OMe)=CH$_2$ could also be obtained by this method.

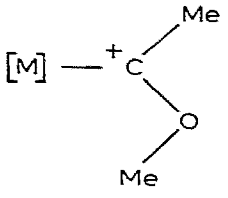
$$[M]\text{—Cl} + \text{Li—C(OMe)=CH}_2 \rightarrow [M]\text{—C(OMe)=CH}_2 \quad (4)$$

The [Pd]—C(OMe)=CH$_2$ complex is a pale brown crystalline solid, which is considerably stable to air and moisture, but it turns black over a period of several months. The [Pt]—C(OMe)=CH$_2$ complex is colorless and much more stable. Both are soluble in dichloromethane, acetone, benzene and ethers, but hardly so in n-hexane, methanol and water.

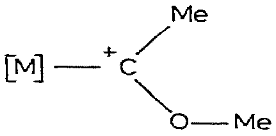
Addition of 60% aqueous perchloric acid to a solution of [Pd]—C(OMe)=CH$_2$ in diethyl ether afforded the expected cationic methyl(methoxy)carbene complex, [Pd]—$^+$C(OMe)Me, in a good yield. In an analogous manner, the platinum complex, [Pt]—C(OMe)=CH$_2$, afforded [Pt]—$^+$C(OMe)Me, which is identical with that prepared from [Pt]—C≡CH.

As was found for [Ni]—$^+$C(OMe)Me [5], treatment of these carbene complexes with triethylamine resulted in the recovery of [Pd]—C(OMe)=CH$_2$ and [Pt]—C(OMe)=CH$_2$, respectively. The C(carbene)—CH$_3$ resonance in the ^{1}H NMR spectra of these carbene complexes in dichloromethane solution readily disappeared on addition of an excess of CH$_3$OD due to H—D exchange. The vinyl complexes, [Pd]—C(OMe)=CH$_2$ and [Pt]—C(OMe)=CH$_2$, also showed analogous H—D exchanges of the vinyl protons.

It was reported previously [5] that the [Ni]—$^+$C(OMe)Me complex has two isomers ($Z : E = 5 : 1$ in dichloromethane) due to the hindered rotation about the C(carbene)—O partial double bond, as shown below:



Z — isomer



E — isomer

The ^1H NMR spectra (Table 1) of [Pd]—$^+C(OMe)Me$ and [Pt]—$^+C(OMe)Me$, however, showed the presence of only one isomer. The phosphine methyl resonance of these complexes consisted of two overlapping 1 : 2 : 1 triplets. The spectral pattern and the chemical shift values are in accord with those of the *Z*-isomer in which the carbene ligand is fixed perpendicularly to the metal coordination plane, perhaps due to the interaction of the methoxy group with the phosphine ligands. The absence of the *E*-isomer in these complexes is tenta-

TABLE 1

IR (cm^{-1}) [a] AND ^1H NMR (ppm) [b] SPECTRAL DATA FOR *TRANS*-$C_6Cl_5M(PPhMe_2)_2R$ AND *TRANS*-$[C_6Cl_5M(PPhMe_2)_2L]ClO_4$ [c]

Complexes R or L	Assignments	M		
		Ni	Pd	Pt
$C(OMe)=CH_2$	$\nu(C=C)$	1578s (1576w)	1582s (1586w)	1585s (1588w)
	$\nu_a(COC)$	1132vs (1138s)	1137s (1138s)	1153s (1153s)
	$\nu_s(COC)$	1017s (1017s)	1018s (1017s)	1025s (1024s)
	$\delta(P—CH_3)$	1.48t(7.7)	1.55t(7.1)	1.65tt(34.4, 7.7)
	$\delta(C=CH)$	3.68dt(2.5, 1.6)	3.66br	3.68br
	$\delta(C=CH)$	4.26dt(3.0, 1.6)	4.47br	4.71br
	$\delta(O—CH_3)$	3.10s	3.28s	3.28s
C(OMe)Me	$\delta(P—CH_3)$	1.55t(8.2) 1.65 t (8.1)	1.65t(7.4) 1.68t(7.7)	1.75tt(33.4, 7.6) 1.77tt(33.4, 7.6)
	$\delta(C—CH_3)$	2.48t(2.3)	2.44br	2.22br
	$\delta(O—CH_3)$	4.64s	4.73s	4.58t(6.8)
C≡CH	$\nu(C—H)$	3280m	3280m	3287m
	$\nu(C≡C)$	1947s	1964s	1973s
	$\delta(P—CH_3)$	1.64t(7.4)	1.72t(7.2)	1.80tt(33.6, 7.7)
	$\delta(C≡CH)$	2.28t(3.8)	2.08t(2.1)	2.11tt(22.6, 2.4)
C≡CPh	$\nu(C≡C)$	2090s	2110s	2110s
	$\delta(P—CH_3)$	1.67t(7.7)	1.76t(7.5)	1.84tt(32.8, 7.4)
Cl	$\delta(P—CH_3)$	1.58t(7.6)	1.64t(7.4)	1.72tt(29.0, 7.4)

[a] In Nujol mull. The dichloromethane solution data are shown in parentheses. [b] In dichloromethane. The coupling constants, J_P, J_H and J_{Pt}, are shown in parentheses in Hz. [c] Some data for the nickel complexes have been reported in ref. 5.

tively attributed to the reduced steric interaction of the methoxy group with the [M] moiety (either M atom itself or an *ortho*-chlorine atom in the pentachlorophenyl group). A stronger metal-to-methoxy proton interaction [11], as well as other electronic preferences, may also explain it.

The phosphine methyl resonance of [Pd]—C(OMe)=CH$_2$ and [Pt]—C(OMe)=CH$_2$ complexes was a single 1 : 2 : 1 triplet, which suggests that in solution the α-methoxyvinyl group is rotating freely around the metal—carbon bond.

Comparison of Brønsted acidities of cationic methyl(methoxy)carbene complexes

The acidity of [Ni]—$^+$C(OMe)Me has been estimated to be comparable with those of the conjugate acids of triethanolamine (pK_a = 7.8) * or 2,4,6-trimethylpyridine (pK_a = 7.4) * [5]. The relative acidities of the [M]—$^+$C(OMe)Me complexes were now estimated by measurements of the ^{1}H NMR spectrum of dichloromethane solution containing one of these carbene complexes and [Ni]—C(OMe)=CH$_2$. The solutions attained equilibrium immediately on mixing (eq. 5).

$$[M]\text{—}^+C(OMe)Me + [Ni]\text{—}C(OMe){=}CH_2 \overset{K}{\rightleftharpoons} [M]\text{—}C(OMe){=}CH_2 + [Ni]\text{—}^+C(OMe)Me \qquad (5)$$

When [Pd]—$^+$C(OMe)Me and [Ni]—C(OMe)=CH$_2$ were mixed in 5 : 3 mole ratio, the spectrum showed the presence of all the four species expected from the equilibrium reaction. The relative ratio of these four species, [Pd]—$^+$C(OMe)Me : [Pd]—C(OMe)=CH$_2$: [Ni]—$^+$C(OMe)Me : [Ni]—C(OMe)=CH$_2$, was ca. 8 : 10 : 10 : 1, and the equilibrium constant of K = 13.2 indicates that [Pd]—$^+$C(OMe)Me is much more acidic than [Ni]—$^+$C(OMe)Me. An analogous equilibrium mixture was obtained by mixing [Pt]—$^+$C(OMe)Me and [Ni]—C(OMe)=CH$_2$ in 1 : 1 mole ratio; the equilibrium constant of K = 0.94 indicates that [Pt]—$^+$C(OMe)Me is slightly less acidic than [Ni]—$^+$C(OMe)Me. These results correlate well with the reactivities of the [M]—C≡CR complexes mentioned above (eq. 2 and 3). That is, the failure of the attempted preparation of [Pd]—$^+$C(OMe)Me by this reaction can be understood by the lesser ability of palladium to form the intermediate cationic vinylidene complex, [Pd]—$^+$C=CH$_2$.

Although it seems reasonable to interpret the highest acidity of [Pd]—$^+$C(OMe)Me in terms of the weakest π-donor ability of palladium to the carbene ligand, this assumption deserves careful inspection to assess its validity, or to explore the other possibilities. An acidity is related to the free-energy change ($\Delta G = \Delta H - T\Delta S$) between the acid and its dissociated system. If the entropy term can be neglected, the acidity of [M]—$^+$C(OMe)Me is a function of the enthalpies of both [M]—$^+$C(OMe)Me and [M]—C(OMe)=CH$_2$ complexes. Accordingly, the higher acidity of [Pd]—$^+$C(OMe)Me, vs. the other two carbene complexes, should be attributed to either a case a) that [Pd]—C(OMe)=CH$_2$ is less destabilized on deprotonation from [Pd]—$^+$C(OMe)Me or a case b) that [Pd]—$^+$C(OMe)Me is less stabilized on protonation to [Pd]—C(OMe)=CH$_2$ than

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* The reported notation for these values in ref. 5 should be replaced by pK_a instead of pK_b.

the other two complexes, or a case c) these factors in combination. A possible origin associated with case a) is the inductive effect of the metals, and that of case b) is the π-donor ability of the metals. In order to obtain information concerning which of these origins explain the acidities most appropriately, a detailed comparison of the individual spectral data is in order.

Comparison of the IR and ^1H NMR spectral data

The IR and ^{1}H NMR spectral data are summarized in Table 1. The $[M]—C(OMe)=CH_2$ complexes in the IR spectra display a characteristic $\nu(C=C)$ band. The frequency increased in the order Ni < Pd < Pt. An analogous progressive increase was observed for the $\nu(COC)$ bands. One of the vinyl proton resonances in the ^{1}H NMR spectra is metal-sensitive and shifts to higher magnetic field in the order Ni > Pd > Pt. In such ways we observed no peculiarity of palladium in the spectral data of $[M]—C(OMe)=CH_2$ complexes, but rather these data are indicative that the M—C bond is polarized, $M^{\delta+}—^{\delta-}C(OMe)=CH_2$ or $M^{\delta+}—C(OMe)=CH_2{}^{\delta-}$, in the order Ni > Pd > Pt. This order parallels the relative electronegativities of these metals at a valency state of two [23]. The phosphine methyl protons of both $[M]—C(OMe)=CH_2$ and $[M]—{}^{+}C(OMe)Me$ series also are magnetically shielded in the same order. That σ-bonding increases in the triad with increasing atomic number of the metal has been shown in several cases where π-bonding is less important. For example, the M—L bond strengths and rates of substitution of low-spin d^8 complexes of type $M^{II}L_4$ decreased in the order Ni > Pd > Pt [24]. The change in isocyanide stretching frequency, $\Delta\nu(C\equiv N)$, on coordination to square planar cationic $MClL_2$ moieties also increased in the same order [25]. d-Orbital splittings in the square planar complexes are generally accepted to increase in this order [26,27].

Turning to the $[M]—{}^{+}C(OMe)Me$ complexes, a reverse order of shielding effect by metals was observed for the $C(carbene)—CH_3$ proton resonance, in which $[Pt]—{}^{+}C(OMe)Me$ complex showed the resonance at more than 0.2 ppm higher magnetic field than the other two complexes. This may reflect the presence of the strongest $d_\pi—p_\pi$ back bonding from the platinum to the carbene carbon atom. There are many studies that have deduced the presence of such π-bonding in platinum(II) complexes. The abnormal high π-donor ability of platinum(II) may have its origin in the d-orbital expansion, of which a theoretical ground exists in the relativity [28]. That π-bonding makes a contribution also to the Ni—C(carbene) bond was shown by the observation of the highest $d—d$ transition energy for $[Ni]—{}^{+}C(OR')Me$ among a variety of complexes of types, $[Ni]—R$ and $[Ni]—{}^{+}L$ [5,8]. Since the chemical shift difference of the $C(carbene)—CH_3$ proton resonances between [Ni]— and $[Pd]—{}^{+}C(OMe)Me$ complexes is very small, it is impossible at present to estimate the relative π-bonding character in the M—C(carbene) bonds. There are some reports of studies of the relative π-donor ability of nickel and palladium at a valency state of two. Otsuka et al. predicted that nickel is a better π-donor to COOR and C(O)R groups than palladium [29], although this bonding mode could not explain the relative reactivity of these complexes. Majima and Kurosawa reported for $[\eta^5\text{-}C_5H_5M(PR_3)(CO)]^+$ complexes that the order of metal to carbonyl π-donation decreased in the order Pt > Ni > Pd [30]. Unfortunately, they made no consideration of the difference in the M—C σ-bonding mode before these conclusions were derived.

Due to the proximity of the C(carbene)—OCH_3 protons to the metal, the chemical shift must be affected by the nonbonding (anti)shielding effect associated with the metal *d*-electrons [31,32] and we leave the discussion until a series of cyclic carbene complexes such as $[M]—^{+}\overline{CCH_2CH_2CH_2O}$ are obtained. The ν(COC) bands expected in the IR spectra of [Pd]— and [Pt]—$^{+}$C(OMe)Me complexes could not be detected, probably due to the weakness and to the presence of many other bands associated with the [M] moieties.

Comparison of the ^{13}C NMR spectral data

The difficulties encountered in the interpretation of ^{13}C NMR spectral data of carbon atoms bonded to different metals have been emphasized [33,34]. A carbon atom bonded directly to a metal atom suffers from a non-bonding shielding effect of the metal, similar to the concept proposed to account for proton chemical shifts in transition metal hydride complexes [35]. In spite of these difficulties, a comparison of ^{13}C NMR spectral data may still be of interest. The $^{13}C\{H\}$ NMR spectral data of relevant carbons for our complexes are summarized in Table 2. The resonances were assigned on the basis of their similarity to data for related parent hydrocarbons [36] and for related platinum complexes [37,38]. The data in the Table reveal that the shieldings of M—C carbon decrease greatly on going from [M]—C(OMe)=CH_2 to [M]—$^{+}$C(OMe)Me complexes, in apparent agreement with the high concentration of the positive charge on the carbon atom. If the non-bonding shielding effects are the same in magnitude for the two types of complexes, the shielding difference, $\Delta\delta$, may be correlated with the change in the M—C bonding mode. Even if the compensation is not complete, it still must be a better parameter than the shielding values themselves. The shielding difference values, which are also shown in the Table, decrease in the order Ni $\geqslant$ Pd $>$ Pt. These results are closely related to

TABLE 2

THE RELEVANT $^{13}C\{H\}$ NMR SPECTRAL DATA (ppm) [a] FOR *TRANS*-$C_6Cl_5M(PPhMe_2)_2R$ AND *TRANS*-$[C_6Cl_5M(PPhMe_2)_2L]ClO_4$ IN CD_2Cl_2

Complexes R or L	Assignments	M = Ni		
		Ni	Pd	Pt
C(OMe)=CH_2	δ(M—C)	174.8t(48.5)	172.3t(24.9)	164.3t(20.6)
	δ(C=CH_2)	90.5t(10.3)	89.5t(13.2)	90.0t(8.1)
	δ(O—CH_3)	54.2s	54.8s	54.4t(37.5)
	δ(P—CH_3)	13.0t(29.4)	13.7t(30.0)	13.1tt(44.1, 38.1)
C(OMe)Me	δ(M—C)	340.8br,s	335.0t(17.9)	310.1br,s
	δ(C—CH_3)	39.1s	41.3s	43.2s
	δ(O—CH_3)	73.0s	73.7s	72.0s
	δ(P—CH_3)	14.3t(33.8)	14.1t(33.8)	13.9t(39.7)
	$\Delta\delta$(M—C)	166.0	162.7	145.8
	$\Delta\delta$(M—C—C)	—51.4	—48.2	—46.8
C≡CH	δ(M—C)	105.4t(83.8)	103.9t(39.0)	96.1t(31.6)
	δ(M—C—C)	104.8s	92.6t(5.9)	94.8tt(254.4, 4.4)
	δ(P—CH_3)	14.5t(30.9)	14.7t(31.6)	14.1tt(43.4, 39.0)

[a] The coupling constants, J_P and J_{Pt}, are shown in parentheses in Hz.

those derived from ^{1}H NMR spectral data, as follows. Since the Ni—C bond of [Ni]—C(OMe)=CH_2 has the largest $M^{\delta+}$—$C^{\delta-}$ σ-bonding polarity and since the positive charge in [Ni]—$^+$C(OMe)Me is less removed to the nickel atom by back π-bonding than that in the platinum complex, the change of charge on the Ni—C carbon must be close to [1 + large δ]. The Pd—C bond polarity in [Pd]—C(OMe)=CH_2 is intermediate and the back π-bonding in [Pd]—$^+$C(OMe)Me is also weaker than that in the platinum complex, and hence the change of charge on the Pd—C carbon is probably close to [1 + intermediate δ]. The polarity in the Pt—C bond in [Pt]—C(OMe)=CH_2 is the smallest and the positive charge in the Pt—C carbon of [Pt]—$^+$C(OMe)Me must be removed considerably (δ') by the presence of the strongest back π-bonding from the platinum, resulting the change of charge close to [1 + small δ — δ']. This relative change of charge on the M—C carbons, therefore, must decrease in the order [Ni]—C > [Pd]—C >> [Pt]—C.

In the above discussion we neglected, for the sake of simplicity, the effects of the M—C σ-bonding polarities in [M]—$^+$C(OMe)Me complexes and the effects of the π-bonding character in the C(carbene)—OMe bond. We believe that the considerations incorporating these effects may not alter significantly the order of the relative change of charge on the M—C carbon among these metals.

The non-bonding shielding effect of metals will be diminished in the other carbon atoms of α-methoxyvinyl and methyl(methoxy)carbene ligands. At the same time these carbons receive less effect by the change of charge between the two types of complexes than the M—C carbons. Therefore, it is probable that the other paramagnetic terms preferentially affect on their chemical shift differences. In fact, the $^+$C(carbene)—*C*H_3 carbon resonances were observed at higher magnetic field than those of corresponding carbon in [M]—C(OMe)=CH_2.

Conclusions

These spectral inspections led us to deduce another interpretation for the relative acidity order observed for [M]—$^+$C(OMe)Me complexes. The lower acidity of [Ni]—$^+$C(OMe)Me (or the higher basicity of [Ni]—C(OMe)=CH_2) than that of [Pd]—$^+$C(OMe)Me is due primarily to the highest σ-bonding polarity in the Ni—C bond of [Ni]—C(OMe)=CH_2, and that of [Pt]—$^+$C(OMe)Me to the strongest π-bonding stabilization of the complex.

Figure 1 represents such a possible free-energy relationship of both [M]—C(OMe)=CH_2 and [M]—$^+$C(OMe)Me complexes. In the Figure the relative free-energies of [M]—C(OMe)=CH_2 complexes were arranged in the order of the metal electronegativities. Those of [M]—$^+$C(OMe)Me were arranged in such a manner that will fit with their acidity relations and spectral relations.

Although we could not obtain any evident information concerning the relative π-bonding strengths between the M—C bonds in [Ni]— and [Pd]—$^+$C(OMe)-Me complexes, there is still a possibility to assign a stronger π-bonding character to the palladium complex. Maitlis has proposed that the oxidation of nickel(II) is much more difficult than that of palladium(II) [26], which implies the possibility. We recently succeeded in the oxidation of [Ni]—Br complex

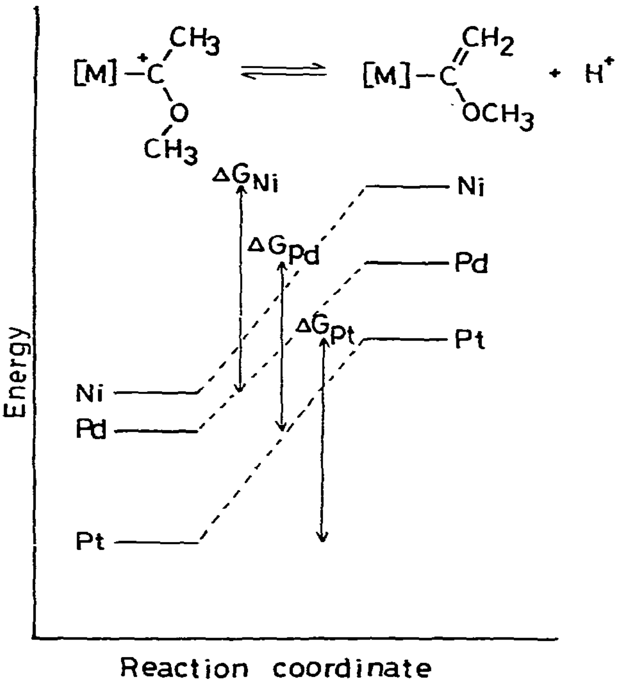

Fig. 1. A qualitative relation between stabilities and Brønsted acidities for [M]—$^{+}$C(OMe)Me and [M]—C(OMe)=CH_2 complexes.

and isolated a nickel(III) complex [39]. When the study is extended to [Pd]— and [Pt]—Br complexes, some valuable informations will be obtained.

Experimental

Infrared spectra were recorded on a Hitachi 215 spectrophotometer. ^{1}H NMR spectra were recorded on a JEOL Model JNM-PS-100 spectrometer operating at 100 MHz using tetramethylsilane as internal standard. $^{13}C\{H\}$ NMR spectra were recorded on a JEOL Model JNM-FX-60S spectrometer operating at 15 MHz using tetramethylsilane as internal standard, and the data are shown in Table 2. The IR and ^{1}H NMR spectral data for some complexes are summarized in Table 1. The nickel complexes in Tables 1 and 2 were prepared as described previously [5]. Melting points and analytical data for new complexes were summarized in Table 3.

Preparation of trans-$C_6Cl_5Pd(PPhMe_2)_2Cl$

An ethereal solution of pentachlorophenyllithium [40] was prepared from hexachlorobenzene (1.024 g, 3.6 mmol) and a 15% n-hexane solution of n-butyllithium (2.2 ml, 3.6 mmol) in 60 ml of dry diethyl ether. The two reagents were mixed at −15 to −20°C under a nitrogen atmosphere to give a pale yellow solution, to which was added *trans*-$Pd(PPhMe_2)_2Cl_2$ (1.36 g, 3 mmol) in small portions at −78°C. The mixture was allowed to warm to room temperature over 2.5 h period, and then was kept stirring for 2 h. The

TABLE 3

ANALYTICAL DATA FOR NEW ORGANO-PALLADIUM(II) AND -PLATINUM(II) COMPLEXES, *TRANS*-$C_6Cl_5M(PPhMe_2)_2R$ AND *TRANS*-$[C_6Cl_5M(PPhMe_2)_2L]ClO_4$

Complexes		M.p. (°C)	Analyses (found (calcd.) (%))		
M	R or L		C	H	Cl
Pd	Cl	188	39.54	3.39	31.85
			(39.59)	(3.32)	(31.87)
Pd	$C{\equiv}CH$	117–118[a]	43.74	3.57	27.19
			(43.87)	(3.53)	(26.98)
Pd	$C{\equiv}CMe$	134–136	45.01	3.77	26.31
			(44.74)	(3.75)	(26.41)
Pd	$C{\equiv}CPh$	126–128	49.27	3.60	24.14
			(49.15)	(3.71)	(24.18)
Pd	$C{\equiv}CCH_2CH_2OH$	119[a]	44.69	3.91	25.04
			(44.54)	(3.88)	(25.28)
Pd	$OClO_3$	159–161[a]	36.02	3.02	29.18
			(36.12)	(3.03)	(29.08)
Pd	$C(OMe){=}CH_2$	122[a]	43.27	4.01	25.70
			(43.58)	(3.95)	(25.72)
Pd	C(OMe)Me	146–147	37.75	3.51	27.10
			(38.03)	(3.57)	(26.94)
Pt	Cl[b]	188–190	34.72	2.83	27.94
			(34.94)	(2.93)	(28.13)
Pt	Cl	179	34.93	2.94	28.05
			(34.94)	(2.93)	(28.13)
Pt	$C{\equiv}CH$	163–166	38.64	3.07	23.59
			(38.65)	(3.11)	(23.77)
Pt	$C{\equiv}CPh$	169–170	43.78	3.14	21.79
			(43.84)	(3.31)	(21.57)
Pt	C(OMe)Me	177–178[a]	34.08	3.23	24.55
			(34.19)	(3.21)	(24.22)
Pt	$C(OMe)CH_2Ph$	138[a]	38.73	3.45	22.36
			(39.02)	(3.38)	(22.29)
Pt	$C(OMe){=}CH_2$	149–150	38.42	3.47	23.00
			(38.61)	(3.50)	(22.79)

[a] Decomposed. [b] *Cis*-complex.

solvent was evaporated and the residue was extracted with dichloromethane/water containing ammonium chloride. The dichloromethane extract was concentrated and chromatographed on a 20-cm column of Florisil utilizing benzene as the eluent. The solvents were evaporated and the residue was recrystallized from acetone to give light yellow crystals of *trans*-$C_6Cl_5Pd(PPhMe_2)_2Cl$ in a yield of 50–75%.

Preparation of cis-$C_6Cl_5Pt(PPhMe_2)_2Cl$

To a stirred solution of pentachlorophenyllithium, prepared from hexachlorobenzene (1.707 g, 6 mmol) and a 15% n-hexane solution of n-butyllithium (3.7 ml, 6 mmol) in 100 ml of dry diethyl ether at −15 to −20°C, was added *cis*-$Pt(PPhMe_2)_2Cl_2$ (2.711 g, 5 mmol) in small portions at −78°C under a nitrogen atmosphere. The mixture was allowed to warm to room temperature over 2.5 h period, and then was stirred for a day, after which the solvents were evaporated. The residue was extracted with dichloromethane/water containing ammonium chloride. The dichloromethane layer was separated, the solvent was evaporated under reduced pressure, and the residue was recrystallized from acetone/methanol to give white crystals of *cis*-$C_6Cl_5Pt(PPhMe_2)_2Cl$ in a yield of 50—75%. The ^1H NMR spectrum (CH_2Cl_2 soln) showed resonances at δ 1.46 (dt, J_{Pt} = 45.2 Hz, J_P = 10.5 Hz) and 1.54 ppm (dt, J_{Pt} = 19.4 Hz, J_P = 9.7 Hz).

Preparation of trans-$C_6Cl_5Pt(PPhMe_2)_2Cl$

A solution of *cis*-$C_6Cl_5Pt(PPhMe_2)_2Cl$ (0.806 g, 1.07 mmol) in 15 ml of acetone containing a catalytic amount (0.0015 ml) of $PPhMe_2$ was refluxed for 6 h under a nitrogen atmosphere. The solution was concentrated to ca. half volume, and was cooled in a refrigerator to give white crystals of *trans*-$C_6Cl_5Pt(PPhMe_2)_2Cl$ in a yield of 0.707 g (88%).

Preparation of trans-$C_6Cl_5Pd(PPhMe_2)_2C{\equiv}CH$

To a solution of *trans*-$C_6Cl_5Pd(PPhMe_2)_2Cl$ (0.334 g, 0.5 mmol) in 10 ml of benzene was added silver perchlorate (0.104 g, 0.5 mmol) in 12 ml of benzene. The mixture was stirred for 0.5 h at room temperature, and the precipitated silver chloride was removed by filtration. The filtrate was placed in a round-bottomed 50-ml flask fitted with a magnetic stirring bar under a nitrogen atmosphere. Triethylamine (0.1 ml) was added, and then gaseous acetylene (34 ml) was bubbled at ca. 5° C. The mixture was stirred for 2 h at ca. 5° C, and then volatile materials were removed under reduced pressure. The residue was washed out with methanol, and was recrystallized from acetone/methanol in a refrigerator to give light brown crystals of *trans*-$C_6Cl_5Pd(PPhMe_2)_2C{\equiv}CH$ in a yield of 0.228 g (69%).

To a solution of *trans*-$C_6Cl_5Pd(PPhMe_2)_2Cl$ (0.03 mmol) and a catalytic amount of cuprous chloride (0.3 mg) in 12 ml of diethylamine was bubbled gaseous acetylene (14 ml) at room temperature under a nitrogen atmosphere. The mixture was stirred for 1 h, and then volatile materials were removed under reduced pressure. The residue was extracted with benzene/water, the benzene layer was separated, and the solvent was removed under reduced pressure. The residue was recrystallized from acetone/methanol as above to give *trans*-$C_6Cl_5Pd(PPhMe_2)_2C{\equiv}CH$ in a yield of 32%.

Preparation of trans-$C_6Cl_5Pd(PPhMe_2)_2C{\equiv}CMe$

To a solution of *trans*-$C_6Cl_5Pd(PPhMe_2)_2Cl$ (0.2 mmol) in 10 ml of acetone was added silver perchlorate (0.2 mmol) in 1 ml of acetone, and the silver chloride precipitate was removed by filtration. Triethylamine (0.04 ml) was added, and the mixture was stirred at 0° C under a nitrogen atmosphere containing gaseous methyl acetylene (200 ml) for 2 h. Volatile materials were removed under reduced pressure, and the residue was recrystallized from acetone/methanol in a refrigerator to give light brown crystals of *trans*-$C_6Cl_5Pd(PPhMe_2)_2C{\equiv}CMe$ in a yield of 80 mg (60%). The IR spectrum (Nujol mull) showed a band due to $\nu(C{\equiv}C)$ at 2118w cm^{-1}, and the ^1H NMR spectrum (CH_2Cl_2 soln) showed resonances at δ 1.71 (t, J_P = 7.4 Hz, P—CH_3) and 1.84 ppm (t, J_P = 2.2 Hz, C—CH_3).

Preparation of trans-$C_6Cl_5Pd(PPhMe_2)_2C{\equiv}CPh$

To a solution of *trans*-$C_6Cl_5Pd(PPhMe_2)_2Cl$ (0.5 mmol) in 10 ml of benzene was added silver perchlorate (0.5 mmol) in 12 ml of benzene. The mixture was stirred for 0.5 h, and the precipitated silver chloride was removed by filtration. To the filtrate were added triethylamine (0.1 ml) and phenylacetylene (0.17 ml, 1.5 mmol) at ca. 5°C under a nitrogen atmosphere. The mixture was stirred at 5°C for 2 h, and then volatile materials were removed under reduced pressure. The residue was recrystallized from benzene/n-hexane or acetone/methanol to give light yellow crystals of *trans*-$C_6Cl_5Pd(PPhMe_2)_2C{\equiv}CPh$ in a yield of 70—75%.

Preparation of trans-$C_6Cl_5Pd(PPhMe_2)_2C{\equiv}CCH_2CH_2OH$

To a solution of *trans*-$C_6Cl_5Pd(PPhMe_2)_2Cl$ (0.5 mmol) in 15 ml of acetone was added silver perchlorate (0.5 mmol) in 7 ml of acetone, and the silver chloride precipitate was removed by filtration. Triethylamine (0.1 ml) and 3-butyn-1-ol (0.06 ml, 0.75 mmol) were added at 0°C under a nitrogen atmosphere, and the mixture was stirred for 2 h at 0°C. Volatile materials were removed under reduced pressure, and the residue was recrystallized from cyclohexane/n-hexane to give light yellow crystals of *trans*-$C_6Cl_5Pd(PPhMe_2)_2C{\equiv}CCH_2CH_2OH$ in a yield of 0.233 g (66%). The IR spectrum (Nujol mull) showed a band due to ν(O—H) at 3490m cm^{-1} and a band due to $\nu(C{\equiv}C)$ at 2116w cm^{-1}, and the ^1H NMR spectrum (CH_2Cl_2 soln) showed resonances at δ 1.67 (t, J_P = 7.5 Hz, P—CH_3), 2.33 (tt, J_H = 6.2 Hz, J_P = 2.1 Hz, CCH_2C) and δ 3.41 ppm (q, J_H = 6.5 Hz, CCH_2O).

Preparation of trans-$C_6Cl_5Pt(PPhMe_2)_2C{\equiv}CH$

To a solution of *trans*-$C_6Cl_5Pt(PPhMe_2)_2Cl$ (0.756 g, 1 mmol) in 60 ml of acetone was added silver perchlorate (0.207 g, 1 mmol) in 10 ml of acetone. The mixture was refluxed for 0.5 h, and the silver chloride precipitated was removed by filtration. The filtrate was placed in a round-bottomed 100-ml flask fitted with a magnetic stirring bar under a nitrogen atmosphere. Triethylamine (0.20 ml) and gaseous acetylene (ca. 1 l) were added with stirring, and the mixture was kept stirring at room temperature overnight. Volatile materials were removed under reduced pressure, and the residue was recrystallized from acetone/methanol to give white crystals of *trans*-$C_6Cl_5Pt(PPhMe_2)_2C{\equiv}CH$ in a yield of 83%.

To a solution of *trans*-$C_6Cl_5Pt(PPhMe_2)_2Cl$ (1 mmol) and a catalytic amount of cuprous chloride (1 mg) in 50 ml of diethylamine was bubbled gaseous acetylene (ca. 200 ml) under a nitrogen atmosphere. The mixture was stirred for a day, and then precipitates were removed by filtration. Volatile materials were removed under reduced pressure, and the residue was recrystallized from acetone/methanol to give *trans*-$C_6Cl_5Pt(PPhMe_2)_2C{\equiv}CH$ in a yield of 73%.

Preparation of trans-$C_6Cl_5Pt(PPhMe_2)_2C{\equiv}CPh$

To a solution of *trans*-$C_6Cl_5Pt(PPhMe_2)_2Cl$ (0.5 mmol) in 30 ml of acetone was added silver perchlorate (0.5 mmol) in 5 ml of acetone. The mixture was refluxed for 0.5 h, and the silver chloride precipitate was removed by filtration. Triethylamine (0.10 ml) and phenylacetylene (0.17 ml, 1.5 mmol) were added to the filtrate under a nitrogen atmosphere with stirring and the mixture was kept stirred overnight. Volatile materials were removed under reduced pressure, and the residue was recrystallized from acetone/methanol to give white crystals of *trans*-$C_6Cl_5Pt(PPhMe_2)_2C\equiv CPh$ in a yield of 0.290 g (71%).

To a solution of *trans*-$C_6Cl_5Pt(PPhMe_2)_2Cl$ (0.05 mmol) and a catalytic amount of cuprous chloride (0.5 mg) in 25 ml of diethylamine was added phenylacetylene (1.5 mmol). The mixture was stirred at room temperature for 24 h, and then precipitates were removed by filtration. Volatile materials were removed under reduced pressure, and the residue was recrystallized from acetone/methanol to give *trans*-$C_6Cl_5Pt(PPhMe_2)_2C\equiv CPh$ in a yield of 87%.

Reaction of trans-$C_6Cl_5Pt(PPhMe_2)_2C\equiv CH$ with perchloric acid in the presence of methanol

To a solution of *trans*-$C_6Cl_5Pt(PPhMe_2)_2C\equiv CH$ (0.149 g, 0.2 mmol) in benzene (3 ml)/methanol (4.5 ml) was added 60% aqueous perchloric acid (0.02 ml, 0.2 mmol) dissolved in 0.5 ml of methanol. The mixture was stirred for a day at room temperature under a nitrogen atmosphere. The solvents were removed under reduced pressure, and the residue was recrystallized from dichloromethane/n-hexane to give white crystals of *trans*-$[C_6Cl_5Pt(PPhMe_2)_2\{C(OMe)Me\}]ClO_4$ in a yield of 0.136 g (77%).

Reaction of trans-$C_6Cl_5Pt(PPhMe_2)_2C\equiv CPh$ with perchloric acid in the presence of methanol

To a solution of *trans*-$C_6Cl_5Pt(PPhMe_2)_2C\equiv CPh$ (0.411 g, 0.5 mmol) in benzene (4 ml)/methanol (3 ml) was added 60% aqueous perchloric acid (0.5 mmol) dissolved in 1 ml of methanol. The mixture was stirred for 20 h under a nitrogen atmosphere, and then the solvent was removed under reduced pressure. The residue was washed with diethyl ether, and was recrystallized from methanol to give white crystals of *trans*-$[C_6Cl_5Pt(PPhMe_2)_2\{C(OMe)CH_2Ph\}]ClO_4$ in a yield of 0.078 g (16%). The ^1H NMR spectrum (CH_2Cl_2 soln) showed resonances at δ 1.62 (tt) and 1.64 (tt, J_{Pt} = 33.3 Hz, J_P = 7.6 Hz, P—CH_3), 3.77 (s, C—CH_2) and 4.78 ppm (t, J_{Pt} = 7.3 Hz).

Reactions of trans-$C_6Cl_5Pd(PPhMe_2)_2C\equiv CR$ (R = H, Me, Ph, CH_2CH_2OH with perchloric acid

trans-$C_6Cl_5Pd(PPhMe_2)_2C\equiv CH$ (0.099 g, 0.15 mmol) was treated with perchloric acid in benzene/methanol in a manner similar to above, but no crystalline material could be isolated.

trans-$C_6Cl_5Pd(PPhMe_2)_2C\equiv CH$ (0.2 mmol) was added to a solution of 60% aqueous perchloric acid (0.2 mmol) in 2 ml of methanol at 0° C under a nitrogen atmosphere. The mixture was stirred at room temperature overnight. Volatile materials were removed under reduced pressure, and the residue was recrystallized from benzene/n-hexane to give white crystals (0.140 g; m.p. 120—122° C), of which the IR spectrum (Nujol mull) showed a band due to OH_2 at 3320 cm^{-1} and bands due to ClO_4^- at 1046, 1110 and 1142 cm^{-1}. The ^1H NMR spectrum (CH_2Cl_2 soln) showed the presence of water (δ 1.94 ppm, s) and benzene. The crystals were kept in a vacuum desiccator for a day to give pure *trans*-$C_6Cl_5Pd(PPhMe_2)_2OClO_3$ in a yield of 75—80%. The IR spectrum (nujol mull) showed bands due to the $OClO_3$ group at 1160—1100br and 1030s cm^{-1}. The ^1H NMR spectrum ($CDCl_3$ soln) showed a resonance at δ 1.75 ppm (t, J_P = 7.1 Hz, $P—CH_3$).

trans-$C_6Cl_5Pd(PPhMe_2)_2C≡CH$, methanol and 60% aqueous perchloric acid (mole ratio = 1 : 6 : 1) were dissolved in acetone-d_6 in an NMR tube. The ^1H NMR spectrum showed a sharp resonance due to free acetylene at δ 2.39 ppm in addition to those due to $P—CH_3$ at δ 1.73 ppm (t), that due to OH at 3.10 ppm (broad) and that due to CH_3O at 3.31 ppm (s).

Analogous results were obtained when the reaction temperature was lowered to —40° C, when the reaction was performed in the presence of free acetylene, and when the other *trans*-$C_6Cl_5Pd(PPhMe_2)_2C≡CR$ compounds were used.

Preparation of trans-$C_6Cl_5Pd(PPhMe_2)_2C(OMe)=CH_2$

Lithiation of methoxy vinyl ether was performed in a round-bottomed 100-ml flask fitted with a magnetic stirring bar and a rubber balloon under a nitrogen atmosphere. To 20 ml of dry tetrahydrofuran was added gaseous methyl vinyl ether (ca. 500 ml) at —50° C, and then a 15% n-hexane solution of n-butyllithium (6.2 ml, 10 mmol) was added. The mixture was allowed to warm to 0° C over a 1 h period, and was kept stirring for 2 h to complete the lithiation. It was cooled again to —50° C, and a solution of *trans*-$C_6Cl_5Pd(PPhMe_2)_2Cl$ (1.33 g, 2 mmol) in 10 ml of dry benzene was added. The mixture was warmed to 0° C over a 1 h period, and was then stirred for 1 h. Cold water containing ammonium chloride was added with stirring over 5 min, and most of the organic solvents were removed under a reduced pressure. The resulting precipitate in water was extracted with diethyl ether. The ether layer was separated, the solvent was evaporated, and the residue was recrystallized from acetone/methanol to give light yellow crystals of *trans*-$C_6Cl_5Pd(PPhMe_2)_2C(OMe)=CH_2$ in a yield of 50—75%.

Preparation of trans-$C_6Cl_5Ni(PPhMe_2)_2C(OMe)=CH_2$ [5] and trans-$C_6Cl_5Pt(PPhMe_2)_2C(OMe)=CH_2$

These complexes were prepared in 65% and 36% yields, respectively, in manners similar to *trans*-$C_6Cl_5Pd(PPhMe_2)_2C(OMe)=CH_2$. The nickel complex has been reported [5], and the platinum complex was identical with that prepared below.

To a suspension of *trans*-$[C_6Cl_5Pt(PPhMe_2)_2\{C(OMe)Me\}]ClO_4$ (0.220 g, 0.25 mmol) in 6 ml of acetone was added triethylamine (0.42 ml) to give a clear solution. Methanol (15 ml) was added and the solution was cooled in a refrigerator to give white crystals of *trans*-$C_6Cl_5Pt(PPhMe_2)_2C(OMe)=CH_2$ in a yield of 0.164 g (84%).

Preparation of trans-$[C_6Cl_5Pd(PPhMe_2)_2\{C(OMe)Me\}]ClO_4$

To a stirred solution of *trans*-$C_6Cl_5Pd(PPhMe_2)_2C(OMe)=CH_2$ (0.345 g, 0.5 mmol) in 5 ml of diethyl ether at 0° C was added dropwise 60% aqueous perchloric acid (0.06 ml, 0.6 mmol). The resulting precipitate (0.369 g) was recrystallized from dichloromethane/n-hexane to give light yellow crystals of *trans*-$[C_6Cl_5Pd(PPhMe_2)_2\{C(OMe)Me\}]ClO_4$ in a yield of 0.324 g (82%).

Preparation of trans-$[C_6Cl_5Pt(PPhMe_2)_2\{C(OMe)Me\}]ClO_4$

In a similar manner as above, this complex was prepared from *trans*-C_6Cl_5Pt-

$(PPhMe_2)_2C(OMe){=}CH_2$ in a yield of 88%. This complex was identical with that prepared from *trans*-$C_6Cl_5Pt(PPhMe_2)_2C{\equiv}CH$.

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