Although Raman and IR modes in the same region may be different in some cases, Table IV indicates that similar trends occur in both Raman and IR bands. Thus, bands II and III increase in frequency on replacement of the proton on N_1 by RHg^{II}, and band II increases in frequency on addition of an electrophile to N_7 when N_1 remains protonated. Band shifts most diagnostic of reaction are I and the IR absorption found at 1540 cm^{-1} in Guo. All species formed with deprotonation at N_1 show a marked decrease in the frequency of I, and the absorption at 1540 cm^{-1} is lowered to 1527–1523 cm^{-1}.

Comparison of the IR and Raman data in Table IV with each other and with those of Table II of ref 11, which includes species with N_7-bound metal, shows that vibrational spectra give a clear indication *only* of the state of protonation of N_1. They alone do not demonstrate whether metal binding is at N_1, N_7, or conceivably O_6.

Registry No. MeHg($GuoH_{-1}$), 68630-40-0; PhHg($GuoH_{-1}$), 68630-41-1; [MeHg(Guo)]NO_3, 68629-63-0; [PhHg(Guo)]NO_3, 68682-88-2; [$(MeHg)_2GuoH_{-1}$]NO_3, 68629-65-2; [$(PhHg)_2GuoH_{-1}$]NO_3, 68629-67-4; [GuoH]NO_3, 68630-42-2; Na[$GuoH_{-1}$], 61393-37-1; PhHg($dThdH_{-1}$), 68630-43-3.

Supplementary Material Available: Table III, NMR data for the ribose group in the complexes (1 page). Ordering information is given on any current masthead page.

References and Notes

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Cationic Carbene Complexes of the (Pentachlorophenyl)nickel(II) Moiety and the Spectrochemical Series of Neutral Carbon Ligands

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A series of stable cationic complexes *trans*-[$C_6Cl_5Ni(PPhMe_2)_2L$]X (L = CNMe, $C(NMeH)_2$, C(NMeH)NMe_2, C(OMe)NMeH, C(OEt)NMeH, C(OMe)NMe_2, and $C(OMe)_2$; X = SO_3F, ClO_4, and PF_6) and *trans*-$C_6Cl_5Ni(PPhMe_2)_2${C(OMe)=NMe} have been prepared. The configuration of these complexes has been assigned on the basis of their ^1H NMR and IR spectra. Their electronic spectra showed a so-called d–d band, and the spectrochemical series of the carbene ligands was discussed with regard to the Ni–C π-bonding properties.

Introduction

There have been extensive studies of the syntheses, spectroscopic properties, and reactivities of transition metal carbene complexes, but reports of nickel carbene complexes are still uncommon compared with reports of palladium and platinum complexes.[1,2] As we previously reported,[3-6] a (pentachlorophenyl)nickel(II) moiety forms a variety of stable cationic complexes of type *trans*-[$C_6Cl_5Ni(PPhMe_2)_2L$]$^+$ (L = neutral ligand), as well as neutral complexes of types *trans*-$C_6Cl_5Ni(PPhMe_2)_2X$ (X = anionic group) and *trans*-$C_6Cl_5Ni(PPhMe_2)_2R$ (R = organic group), and we have recently reported[7,8] the syntheses of a series of stable cationic carbene complexes of types *trans*-[$C_6Cl_5Ni(PPhMe_2)_2${C(OR′)Me}]$^+$ and *trans*-[$C_6Cl_5Ni(PPhMe_2)_2${C(OMe)C_6H_4Y-*p*}]$^+$. Characteristic for these nickel complexes is the observation in the electronic spectrum of a band attributable to the so-called d–d transition.[5,6,8] We present here additional examples of stable cationic carbene complexes of the same nickel moiety and investigate the spectrochemical series of carbene ligands with a hope to elucidate their bonding properties.

Experimental Section

Since methyl fluorosulfonate has been cited[9] to be extremely toxic, experimental work using this reagent was performed in a hood. The commercial grade reagent was used after distillation under a nitrogen atmosphere. IR spectra were recorded on a Hitachi 225 spectrophotometer or on a Hitachi 215 spectrophotometer over the range 4000–650 cm^{-1} and on a Hitachi EPI-L spectrophotometer over the

Table I. Analytical Data for New Nickel Complexes *trans*-$[C_6Cl_5Ni(PPhMe_2)_2L]X$ and *trans*-$C_6Cl_5Ni(PPhMe_2)_2R$

complexes			% C found (calcd)	% H found (calcd)	% N found (calcd)	conductivity, Ω^{-1} cm^2 mol^{-1}				^{1}H NMR in CH_2Cl_2,^{b,c} δ(P–CH_3), ppm
no.	L or R	X				in CH_2Cl_2^{a}		in $(CH_3)_2CO$^{a}		
						10^{-3} M	10^{-4} M	10^{-3} M	10^{-4} M	
1a	CNMe	SO_3F	39.79 (39.87)	3.48 (3.43)	1.93 (1.88)	25.5	53.8	142	164	1.69 t
1b	CNMe	ClO_4				25.1	52.4			1.69 t
1c	CNMe	PF_6				28.4	58.7			1.68 t
2a	$C(NMeH)_2$	PF_6	37.62 (37.47)	3.92 (3.77)	3.40 (3.50)	12.7	30.9	141	158	1.47 t 1.54 t
2b	$C(NMeH)NMe_2$	PF_6	38.56 (38.30)	4.12 (3.96)	3.22 (3.44)	21.2	41.9			1.39 t 1.61 t
3	C(OMe)=NMe		45.73 (45.74)	4.29 (4.30)	2.10 (2.13)					1.45 t 1.52 t
4a	C(OMe)NMeH	ClO_4	39.80 (39.67)	3.82 (3.86)	1.91 (1.85)	10.2	23.6	138	164	1.52 t 1.55 t
4b	C(OEt)NMeH	ClO_4	40.22 (40.51)	4.11 (4.05)	1.80 (1.82)	11.2	23.6			1.45 t 1.48 t
4c	$C(OMe)NMe_2$	ClO_4	40.30 (40.51)	4.05 (4.05)	1.79 (1.82)	38.3	71.6			1.50 t 1.60 t
5	$C(OMe)_2$	PF_6	37.45 (37.38)	3.51 (3.51)		39.5	71.5	147	164	1.36 t 1.74 t

[a] At 25 °C. [b] At 23 °C, except for **5** (−25 °C). [c] t: 1:2:1 triplet with J_P = ca. 7–8 Hz.

range 700–200 cm^{-1}. ^{1}H NMR spectra were recorded on a Jeol Model JNM-PS-100 spectrometer operating at 100 MHz. Chemical shifts were measured relative to Me_4Si as an internal standard. Electronic spectra were measured on a Hitachi Model 200-20 spectrophotometer at 25 ± 0.1 °C. Analytical data for new complexes are summarized in Table I.

Preparation of *trans*-$C_6Cl_5Ni(PPhMe_2)_2CN$. To a solution of *trans*-$C_6Cl_5Ni(PPhMe_2)_2Cl$ (6.20 g, 10 mmol) in 200 mL of acetone was added sodium cyanide (0.542 g, 11 mmol) in 20 mL of water. The solvent was removed on a boiling water bath as far as possible, and 100 mL of dichloromethane was added to extract the yellow-brown residue. The dichloromethane layer was filtered if turbid, and 150 mL of *n*-hexane was mixed in. The mixture was concentrated on a water bath to ca. half volume and was cooled to give orange-yellow crystals of *trans*-$C_6Cl_5Ni(PPhMe_2)_2CN$, in a yield of 5.75 g (94%), mp 197–198 °C (reported,[5] 196–198 °C). The IR and ^{1}H NMR spectra were identical with those of a sample prepared previously[5] from *trans*-$C_6Cl_5Ni(PPhMe_2)_2OOCCH_3$.

Preparation of *trans*-$[C_6Cl_5Ni(PPhMe_2)_2CNMe]X$ (X = SO_3F, 1a; X = ClO_4, 1b; X = PF_6, 1c). To a solution of *trans*-$C_6Cl_5Ni(PPhMe_2)_2CN$ (3.05 g, 5.0 mmol) in 75 mL of dry benzene was added 0.5 mL of methyl fluorosulfonate under nitrogen atmosphere. The mixture was stirred at room temperature overnight to give a yellow precipitate, which was filtered in air and recrystallized from ethanol to give **1a**, in a yield of 2.64 g (73 %), mp 194–196 °C.

Addition of an excess of NH_4ClO_4 to a methanol solution of **1a** resulted in the precipitation of **1b**, in a yield of 86%, mp 212–214 °C. Similarly, **1c** was obtained in a yield of 88%, mp 194–196 °C.

Preparation of *trans*-$[C_6Cl_5Ni(PPhMe_2)_2\{C(NMeH)_2\}]PF_6$ (2a). To a suspension of **1c** (0.385 g, 0.5 mmol) in 30 mL of isopropyl alcohol was added 0.8 mL of 40% aqueous methylamine under nitrogen atmosphere. The mixture was heated to 75 °C to give a clear solution and was kept for 2 h. It was filtered while hot in air. The filtrate was cooled in a refrigerator to give cream yellow crystals of **2a**, in a yield of 0.240 g (60%), mp 212–225 °C dec.

Preparation of *trans*-$[C_6Cl_5Ni(PPhMe_2)_2\{C(NMeH)NMe_2\}]PF_6$ (2b). To a suspension of **1c** (0.385 g, 0.5 mmol) in 10 mL of isopropyl alcohol was added 1 mL of 40% aqueous dimethylamine under nitrogen atmosphere. The mixture was treated in a similar manner as above to give cream yellow crystals of **2b**, in a yield of 35–51%, mp 201–204 °C dec.

Preparation of *trans*-$C_6Cl_5Ni(PPhMe_2)_2\{C(OMe){=}NMe\}$ (3). To a suspension of **1c** (0.770 g, 1 mmol) in 25 mL of methanol was added a 2 mmol solution of sodium methoxide in 3 mL of methanol. The resultant orange solution was stirred overnight at room temperature, and then the solvent was removed under reduced pressure. Recrystallization of the residue from *n*-hexane gave orange crystals of **3**, in a yield of 0.343 g (52 %), mp 130–132 °C dec.

Preparation of *trans*-$[C_6Cl_5Ni(PPhMe_2)_2\{C(OMe)NMeH\}]ClO_4$ (4a). To a solution of **3** (0.328 g, 0.5 mmol) in 10 mL of ethanol was added 0.05 mL (0.5 mmol) of 60% aqueous perchloric acid. The resultant precipitate was filtered, washed with methanol, and dried in air to give **4a**, in a yield of 0.352 g (93%), mp 189–190 °C dec.

Preparation of *trans*-$[C_6Cl_5Ni(PPhMe_2)_2\{C(OEt)NMeH\}]ClO_4$ (4b). To a suspension of **1b** (0.724 g, 1 mmol) in 20 mL of ethanol was added a 2 mmol solution of sodium ethoxide in 3 mL of ethanol. The mixture was stirred overnight at room temperature and then was filtered. The filtrate was concentrated under reduced pressure to ca. half volume. Addition of a few drops of 60% aqueous perchloric acid resulted in the precipitation of cream yellow crystals, which were filtered, washed with ethanol, and dried in air to give **4b**, in a yield of 0.641 g (83%), mp 191–192 °C.

Preparation of *trans*-$[C_6Cl_5Ni(PPhMe_2)_2\{C(OMe)NMe_2\}]ClO_4$ (4c). To a solution of **3** (1.312 g, 2 mmol) in 20 mL of dry benzene was added 0.2 mL of methyl fluorosulfonate under nitrogen atmosphere. The mixture was stirred at room temperature overnight. The resultant precipitate was filtered and dissolved in methanol (10 mL). Addition of 3 mL of a methanol solution of NH_4ClO_4 (2 mmol) resulted in the formation of cream yellow crystals of **4c**, in a yield of 0.731 g (47 %), mp 229–231 °C.

Preparation of *trans*-$C_6Cl_5Ni(PPhMe_2)_2COOMe$. To a solution of *trans*-$C_6Cl_5Ni(PPhMe_2)_2Cl$ (2.48 g, 4 mmol) in 40 mL of acetone was added silver perchlorate (0.829 g, 4 mmol) in 10 mL of acetone. The silver chloride precipitate was removed by filtration, and the filtrate was dried under reduced pressure. The residue was dissolved in 70 mL of dry methanol under an atmosphere of carbon monoxide. The solution was stirred vigorously at 0 °C for ca. 1 h to give a light yellow precipitate of *trans*-$[C_6Cl_5Ni(PPhMe_2)_2CO]ClO_4$.[5] Addition of triethylamine (1 mL) gave at once a clear solution and subsequently precipitation of *trans*-$C_6Cl_5Ni(PPhMe_2)_2COOMe$, in a yield of 2.06 g (80%), which was recrystallized under carbon monoxide atmosphere from methanol, mp 142–144 °C (reported,[5] 144–146 °C).

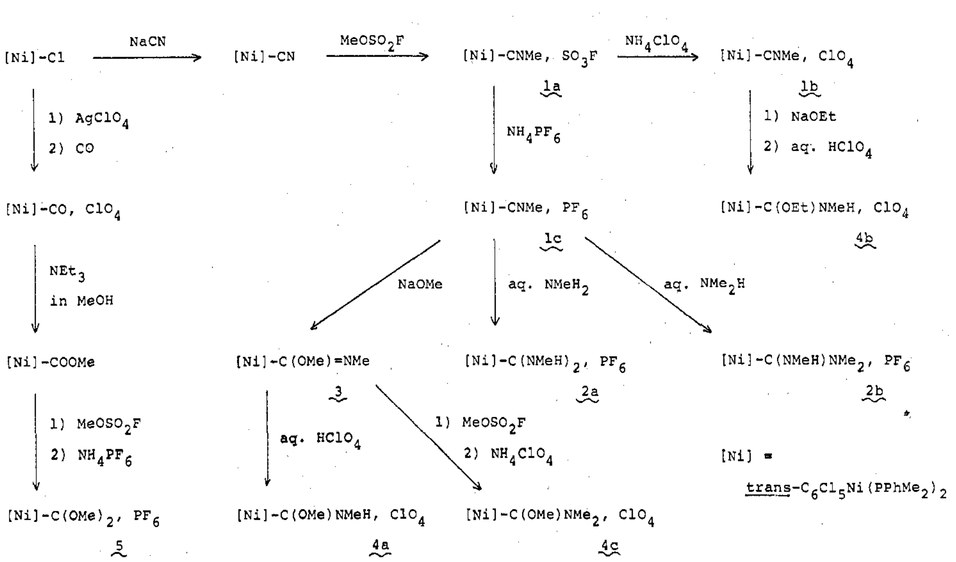
Preparation of *trans*-$[C_6Cl_5Ni(PPhMe_2)_2\{C(OMe)_2\}]PF_6$ (5). To a solution of *trans*-$C_6Cl_5Ni(PPhMe_2)_2COOMe$ (1.287 g, 2 mmol) in 25 mL of dry benzene was added 0.8 mL of methyl fluorosulfonate under nitrogen atmosphere. The mixture was stirred at room temperature overnight. The resultant precipitate was filtered and dissolved in methanol (15 mL). Addition of 5 mL of methanol solution of NH_4PF_6 (2 mmol) resulted in the formation of yellow needle crystals of **5**, in a yield of 0.796 g (50%), mp 176–178 °C dec.

Results and Discussion

The preparative routes for new (pentachlorophenyl)nickel(II) complexes **1a–c**, **2a,b**, **3**, **4a–c**, and **5** are summarized in Scheme I. The complexes thus obtained are very stable in air both in the solid state and in solution at room temperature.

^{1}H NMR Spectra. The ^{1}H NMR spectra show resonances arising from the phosphine ligands (Table I) and the carbon

Scheme I



ligands (Figure 1), where the resonance positions and coupling constants are assigned to the established configurations of the carbon ligands.

The single 1:2:1 triplet pattern of phosphine methyl protons observed for methyl isocyanide complexes **1a–c** is typical of a trans square-planar configuration. The spectra of **2a**,**b** **3**, and **4a–c** show, on the other hand, a double 1:2:1 triplet pattern. This indicates that these complexes have a trans configuration with no plane of symmetry through the P–Ni–P system.[10] Therefore there must be a restricted rotation about the Ni–C bond with the ligand oriented perpendicularly to the nickel coordination plane. The feature of this restricted rotation about the Ni–C bond is in contrast with the observation for *trans*-$[PtCl(PPhMe_2)_2\{C(NMeH)_2\}]ClO_4$ and *trans*-$[PtCl(PPhMe_2)_2\{C(NMeH)NMe_2\}]ClO_4$ reported by Crociani and Richards,[11] who found free rotation about the Pt–C bonds. A covalent radius of 1.18 Å for Ni(II) has been proposed by Fahey[12] and of 1.31 Å for Pt(II),[13] and thus the nickel complexes must have a shorter M–C bond and enough M–P bonds to restrict the carbon–ligand rotation. In our recent work,[6] we found that even the *m*-tolyl group, as well as the *o*-tolyl group, in *trans*-$C_6Cl_5Ni(PPhMe_2)_2$(tolyl) is fixed perpendicularly to the nickel coordination plane. The presence of partial d_π–p_π bond character in the Ni–C(carbene) bond is discussed below. This influence as the origin for the perpendicular orientation, however, is excluded because of the cylindrical distribution of nickel d orbitals. This would produce, probably, a very small rotational barrier, if any.

The electronic configuration of the cationic carbene complexes might be represented as a resonance hybrid of four

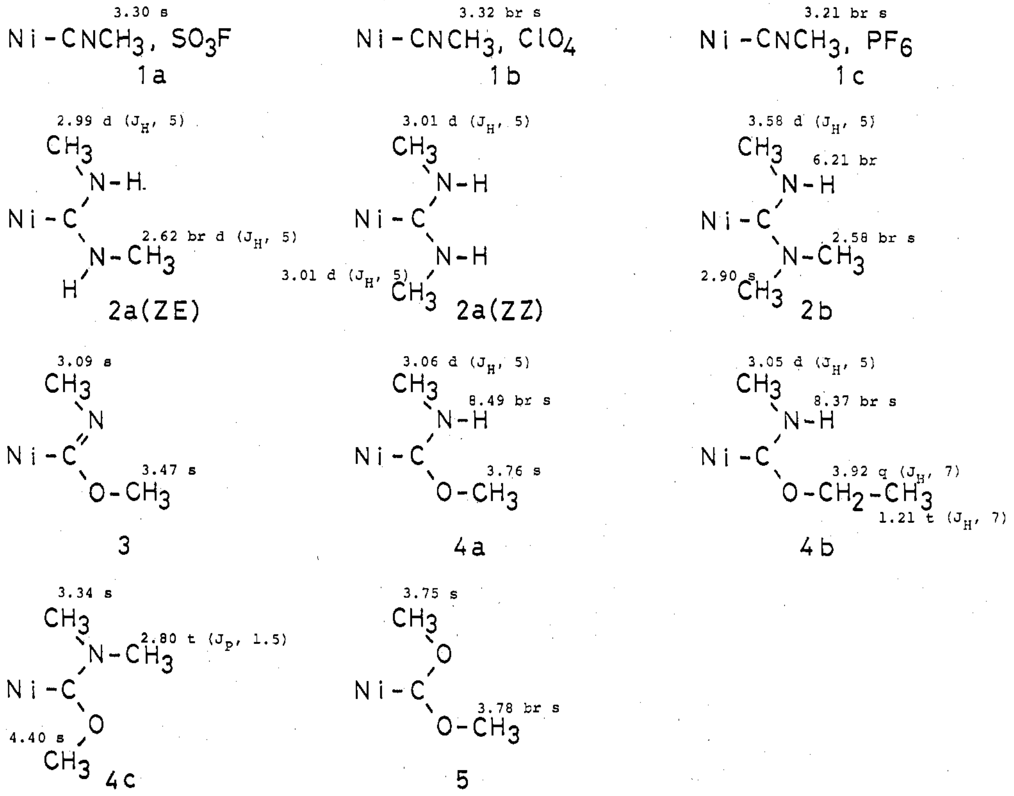
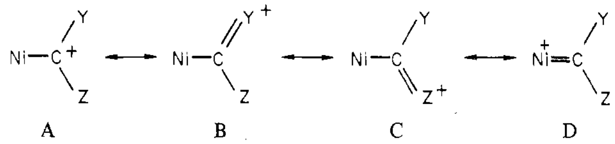


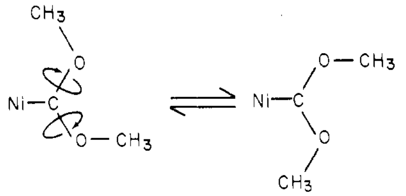
Figure 1. ^1H NMR data for carbon ligands bonded to the *trans*-$C_6Cl_5Ni(PPhMe_2)_2$ moiety ($CDCl_3$ solution at 23 °C except for **5**, CH_2Cl_2 solution at −25 °C; the chemical shifts, δ, are in ppm from Me_4Si, and the J_H and J_P values are in Hz; abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; br, broad).

limiting structures A–D, where Y, Z = NMeH, NMe_2, OMe,



or OEt. The nonequivalence of methyl groups in the dimethylamino group of **2b** and **4c** is attributable to the presence of double-bond character between the C(carbene)–N bond. For the establishment of carbon–ligand configuration shown in Figure 1, we used the criterion that the methyl group trans to the (pentachlorophenyl)nickel moiety with respect to C-(carbene)–N bonds should show the resonance broadened by the presence of ^5J_P. The results are in good agreement with the presumption that the methyl group cis to the nickel moiety suffers from the magnetic anisotropy of the nickel(II) atom to give the resonance at lower magnetic field.[14] Noteworthy is the observation for **2a** that the spectrum is time dependent. The fresh deuteriochloroform solution shows the presence of only a *ZE* isomer (see Figure 1), thus the isomer in the solid state. As time progresses a new doublet resonance due to the *ZZ* isomer appears in the spectrum, and in 2 h it attains equilibrium with ca. 30% *ZZ* isomer. An analogous spectrum is observed for the dichloromethane solution attaining equilibrium with ca. 20% *ZZ* isomer, but in deuterioacetone the equilibrium lies completely to the *ZE* isomer. The solvent dependence in the isomer distribution is reported also for the above Pt(II) complexes.[11] The configuration of the alkoxy group in each of **3** and **4a,b** is uncertain, and there are possibilities of *ZZ* configuration as well as of free rotation about the C(carbene)–O bond. However, an *EZ* configuration, in which the *N*-methyl group is trans to the nickel moiety, can be excluded according to the above mentioned criterion, although this configuration has been found[15] by X-ray crystallography of *cis*-$PdCl_2\{C(OMe)NMeH\}_2$.

Complex **5** is the first example of a dimethoxycarbene complex, other dialkoxycarbene complexes having been reported quite recently.[16] The ^1H NMR spectrum of **5** is temperature dependent, showing two resonances for both phosphine methyl and methoxy methyl protons at temperatures lower than 23 °C and one resonance at higher temperatures. These results may be best explained by assuming that the dimethoxycarbene ligand is of *ZE* configuration and is fixed perpendicularly to the coordination plane below 23 °C but is fluxional at higher temperature by free rotation about the C(carbene)–O bonds, as shown below.



The N–H proton resonance is observed for **2b**, **4a**, and **4b** in deuteriochloroform or dichloromethane as a very broad signal. The large chemical shift differences between **2b** and **4a,b** might be related to the higher acidity of **4a,b** over **2b**, as is evident from the following IR spectra and conductivity measurements.

IR Spectra and Conductivities. The characteristic IR absorptions of complexes studied are shown in Table II. Coordinated methyl isocyanide has $\nu(C{\equiv}N)$ at a higher position relative to the free ligand (2170 cm^{-1}),[17] as is usually observed for the isocyanide complexes of metals in oxidation state I or higher.[18]

The imino complex **3** has a band at 1588 cm^{-1} assigned to $\nu(C{=}N)$ and bands at 1129 and 1068 cm^{-1} assigned to ν(COC). In the protonated complex **4a** these bands shift to lower and higher frequency regions, respectively, which is indicative of the importance of resonance structure C (Y = NMeH and Z = OMe), as well as of B, in the complex.

Table II. IR Spectral Data for *trans*-$[C_6Cl_5Ni(PPhMe_2)_2L]X$ and *trans*-$C_6Cl_5Ni(PPhMe_2)_2R$, in cm^{-1}

complexes	assignments	Nujol	CH_2Cl_2 soln
1a	$\nu(C{\equiv}N)$	2222 vs	
	SO_3F^-	1275 vs, 1062 s, 581 s	
1b	$\nu(C{\equiv}N)$	2227 vs	
	ClO_4	1090 vs, 630 s	
1c	$\nu(C{\equiv}N)$	2225 vs	
	PF_6	840 vs, 560 s	
2a	$\nu(N{-}H)$	3433 m, 3382 m	3422 m, 3364 m
	$\nu(C\underset{..}{-}N)$	1579 s	1568 s
	$\delta(N{-}H)$	1519 m	1505 m
	PF_6^-	830 vs, 560 s	
2b	$\nu(N{-}H)$	3380 m	3380 m
	$\nu(C\underset{..}{-}N)$	1561 s	1566 s
	PF_6^-	828 vs, 560 s	
3	$\nu(C{=}N)$	1588 s	1588 s
	$\nu(COC)$	1129 s, 1068 vs	
4a	$\nu(N{-}H)$	3240 m, br	3241 m, br
	$\nu(C\underset{..}{-}N)$	1580 s	1572 s
	$\nu(COC)$	1248 s	
	ClO_4^-	1110 vs, 1075 sh, 625 s	
4b	$\nu(N{-}H)$	3230 m, br	3248 m, br
	$\nu(C\underset{..}{-}N)$	1573 s	1570 s
	$\nu(COC)$	1227 s	
	ClO_4^-	1095 vs, 626 s	
4c	$\nu(C\underset{..}{-}N)$	1565 s	
	$\nu(COC)$	1282 s and/or 1226 m	
	ClO_4^-	1090 vs, 626 s	
5	$\nu(COC)$	(1284 s)[a]	
	PF_6^-	840 vs, 559 s	

[a] Overlapped with bands due to C_6Cl_5 vibrations.

The ν(N–H) frequencies of the amino(alkoxy)carbene complexes **4a,b** are low in comparison with those of the diamino carbene complexes **2a,b**. Analogous observations are reported for platinum(II) complexes by Badley, Chatt, and Richards.[17] They attributed this result to the higher contribution of the resonance structure with a positive charge on nitrogen than that on oxygen of amino(alkoxy)carbene complexes. Their explanation seems to be supported by the conductivity measurement of the present nickel complexes (Table I). Complexes **4a,b** show the lowest conductivities in dichloromethane due to the strongest hydrogen bond between the N–H proton and the counteranion. The highest conductivity is obtained for **4c** and **5**. In acetone all the cationic nickel complexes show analogous conductivity values.

Electronic Spectra. The electronic spectral data for the cationic nickel carbene complexes and their precursors are given in Table III. With corresponding bands observed for a variety of complexes of types *trans*-$C_6Cl_5Ni(PPhMe_2)_2X$ and *trans*-$[C_6Cl_5Ni(PPhMe_2)_2L]ClO_4$, the variation in λ_{max} with changes in coordinating atom of the ligand (X or L) has been shown to follow a well-known spectrochemical series,[5] indicating that the transition is predominantly from filled d_{xy} to unfilled $d_{x^2-y^2}$ (σ^*) orbitals. The spectra of carbene complexes show the band in a higher energy region than that observed previously for *trans*-$C_6Cl_5Ni(PPhMe_2)_2R$ (R = aryl,[6,8] 358–382 nm). This observation can be explained as caused either by (i) a stronger σ-donating property of the carbene ligands than the aryl group, to raise the $d_{x^2-y^2}$ (σ^*) orbital, by (ii) a stronger π-accepting property to lower the d_{xy} orbital, or by (iii) the combination of (i) and (ii). The trend observed for carbene complexes is that electron-richer carbene ligands are weaker in the apparent ligand field strength and therefore

Table III. Electronic Spectral Data for *trans*-$[C_6Cl_5Ni(PPhMe_2)_2L]X$ and *trans*-$C_6Cl_5Ni(PPhMe_2)_2R$

complexes		λ_{max}, nm (ϵ)[a]		
no.	L or R	in CH_2Cl_2	in $(CH_3)_2CO$	ref
	CN	356 (829)		5
	CO	363 (sh)[b]		5
	COOMe	340 (sh)		5
1a	CNMe	352 (1606)	352 (1593)	this work
1b	CNMe	353 (1613)		this work
1c	CNMe	353 (1616)		this work
2a	$C(NMeH)_2$	351 (798)	350 (806)	this work
2b	$C(NMeH)NMe_2$	355 (757)		this work
3	C(OMe)=NMe	353 (sh)		this work
4a	C(OMe)NMeH	347 (974)	348 (1006)	this work
4b	C(OEt)NMeH	347 (927)		this work
4c	$C(OMe)NMe_2$	352 (903)		this work
5	$C(OMe)_2$	343 (1614)	343 (sh)	this work
	C(OMe)Me	332 (sh)		7, 19
	C(OEt)Me	332 (sh)		7, 19
	C(O-*n*-Pr)Me	335 (sh)		7, 19

[a] The spectra exhibited very intense bands in the ultraviolet region tailing toward the visible region. The total ϵ values are shown here. [b] Measured for Nujol mull.

can be explained only by assuming the presence of Ni–C(carbene) π bonding (or resonance D), which becomes stronger as the carbene ligand becomes electron poorer.

The above conclusion agrees well with the results reported by a number of workers studying with different physical methods that diaminocarbene[20-22] and amino(alkoxy)carbene[22,23] ligands are weak π acceptors, that the dialkoxycarbene ligand is a stronger π acceptor than diaminocarbene,[16a] that alkyl(alkoxy)carbene ligands are either weak π acceptors[24-26] or moderate to strong π acceptors,[27,28] and that methylene,[29] CHR,[29] and diphenylcarbene[30] are strong π acceptors.

Although the results in Table III indicate that the carbene ligands are apparently at a higher position in the spectrochemical series than CN^- and CO, it is difficult to compare from these data the total amount of Ni–C π-bond character. This is so not only because of the difference in the σ-orbital hybridization (sp^2 or sp) which effects the $d_{x^2-y^2}$ (σ^*) orbital but also because of the cylindrical property of the latter ligands, i.e., that the two nickel d_π orbitals can participate in the π bonding.

Registry No. **1a**, 68550-26-5; **1b**, 68550-27-6; **1c**, 68568-34-3; **2a**, 68550-29-8; **2b**, 68550-31-2; **3**, 68550-32-3; **4a**, 68550-34-5; **4b**, 68550-36-7; **4c**, 68550-38-9; **5**, 68550-40-3; [Ni]-CN, 59991-83-2; [Ni]-Cl, 15526-04-2; [Ni]-COOMe, 59982-61-5.

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An Extensive Trans-Effect Series: The Reaction of Coordinated Trimethyl Phosphite

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The rate of reaction of Br^- with $(CH_3O)_3PCo(DH)_2X$ to form $(CH_3O)_2P(O)Co(DH)_2X$ (where DH = monoanion of dimethylglyoxime) varies by a factor of 10^5 as X is varied from NO_3 to C_2H_5. The log of the observed rate constant for this reaction correlates very well with the ^{13}C chemical shift of the phosphite carbon. Comparisons are made between the effects of the X group on ligand substitution reaction and on the reaction of the coordinated phosphite. A hypothesis is presented proposing that the steric bulk of X may influence the ability of X to act as an electron donor to the metal center. In contrast to some studies on ligand substitution reactions, our results do not correlate well with the Hammett substituent constants σ_p and σ_p^-.

Recently, there has been great interest in the study of how the variation of both neutral (L) and negative (X) ligands affects structural, spectroscopic, and rate parameters of both transition- and non-transition-metal complexes.[1-3] It now appears that the influence of either L or X ligands is frequently roughly transferable, i.e., is independent of the metal moiety.[1-3]

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