

Isolation and Methylation of Arylnickel Intermediates Derived by Carbonylation of *trans*-Aryl(pentachlorophenyl)bis(phenyldimethylphosphine)nickel(II) Compounds

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From the reaction of *trans*-C₆Cl₅Ni(PPhMe₂)₂C₆H₄X-*p* (**1**) with carbon monoxide, three arylnickel(II) complexes, *trans*-C₆Cl₅Ni(PPhMe₂)₂C(O)C₆H₄X-*p* (**2**) (X = a, N(CH₃)₂; b, OCH₃; c, CH₃), were isolated. These complexes, **2**, react further with carbon monoxide to give C₆Cl₅C(O)C₆H₄X-*p* (**3**) but thermally decompose to give C₆Cl₅C₆H₄X-*p* (**5**). Methylation by methyl fluorosulfonate occurred at the aryl oxygen atom of **2** to give cationic aryl(methoxy)carbenenickel(II) complexes, *trans*-[C₆Cl₅Ni(PPhMe₂)₂{C(OCH₃)C₆H₄X-*p*}]⁺ (**4**). The IR, ¹H NMR, and electronic spectra of **2** were explained with the contribution of resonance forms having an anionic charge on the aryl oxygen atom. The carbene complexes, **4**, are stable thermally, and their ¹H NMR spectra showed a perpendicular relationship between the plane of the carbene ligand and the nickel coordination plane.

Introduction

Carbon monoxide insertion into a transition metal-carbon bond has been widely studied,¹ because of its relevance to many organic syntheses. We have recently reported² that carbon monoxide reacts readily at room temperature and normal pressure with some thermally stable arylnickel(II) complexes of the type *trans*-C₆Cl₅Ni(PPhMe₂)₂C₆H₄X (**1**). The isolated products were characterized as aryl(pentachlorophenyl) ketones, C₆Cl₅C(O)C₆H₄X (**3**).

The possible intermediate of the reaction is expected to be arylnickel(II) complexes, **2**, as shown in Scheme I. Here we report studies on the isolation of these intermediates and their reactions with methyl fluorosulfonate to give cationic aryl(methoxy)carbenenickel(II) complexes, **4**. Some spectroscopic investigations of these complexes will also be reported.

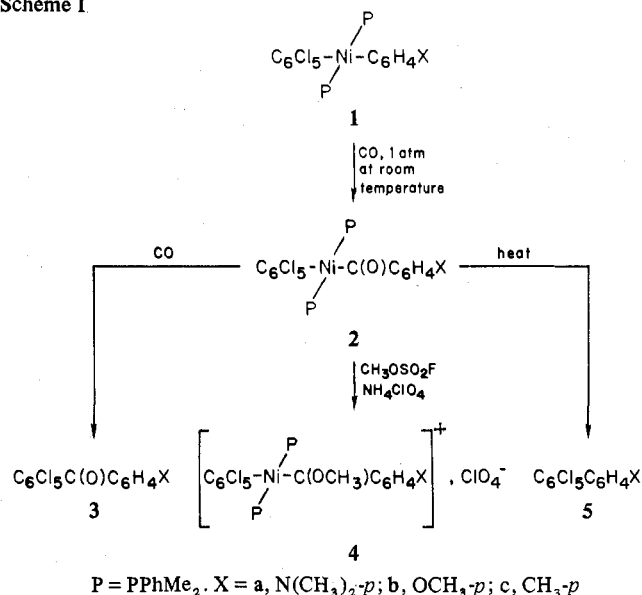
Results and Discussion

Isolation of Arylnickel(II) Intermediates. Treatment of an acetone solution of **1a** with carbon monoxide at 0 °C resulted in less than 1 h in precipitation of the arylnickel(II) complex **2a** with a good yield. From the reaction mixture of **1b** or of **1c** in dichloromethane, the corresponding arylnickel complexes **2b** and **2c** could also be isolated. The best yields of **2b** and **2c** were attained on 2- or 2.5-h treatments at 20 °C, respectively, but they were still considerably poorer than that of **2a**. Several attempts to isolate the other arylnickels from **1d** or **1e** (X = d, H; e, Cl-*p*) have failed. The failure may be attributed to the low concentrations of the intermediates during these reactions. This is probably due to the decreased rate of carbon monoxide insertion relative to the rate of reductive elimination of **2d** and **2e**. Garrou and Heck reported recently³ that electron-withdrawing para substituents in the phenyl group attached to a palladium decrease the reaction rate of carbon monoxide insertion.

The arylnickel complexes **2a-c** thus isolated are moderately stable in the solid state at room temperature but decompose spontaneously on heating at ca. 110 °C. From the solution of **2a** in tetrachloroethylene heated at 100 °C were isolated C₆Cl₅C₆H₄N(CH₃)₂-*p* (**5a**) and *trans*-(CCl₂=CCl)Ni(PPhMe₂)₂Cl. The IR spectra of **2a-c** heated at 110 °C in Nujol showed the presence of **5**, but the ketones **3** could not be detected. This is a good indication that a thermal decarbonylation of **2** occurred first, followed by a reductive elimination. Under carbon monoxide, **2a-c** decomposed slowly at room temperature to give their reductive elimination products, **3**.

Several acylnickel complexes have recently been made,⁴⁻⁷ but few arylnickel derivatives have been isolated analytically pure.^{3,7-10} These well-characterized acylnickel complexes display in the IR spectra a characteristic ν(CO) band in the

Scheme I



region 1660–1620 cm⁻¹. The IR spectra of **2a-c**, however, showed no band in the normal ν(CO) region of 1750–1600 cm⁻¹, but three medium to strong bands in the region of 1600–1500 cm⁻¹. These data are shown in Table I. The band at ca. 1600 cm⁻¹ is commonly observed in the spectra of complexes **1** and **2** and can be attributed to the aryl ring vibration. Accordingly, there are two choices for assignment of the ν(CO) band: both of the remaining two bands or one of them excluding the band observed constantly at 1560–1550 cm⁻¹. The latter choice is tentatively adopted in Table I, and the spectral data are shown without parentheses. It is apparent that the band shifts to higher frequency region on the change of the para substituent from dimethylamino to methoxy or methyl groups. In spite of the uncertainty in the assignment, these ν(CO) values suggest high electron density on the aryl oxygen atom and are in fact in a region more normally associated with transition metal-acylate species.¹¹⁻¹³ The extensive delocalization on to the aryl oxygen would be explained by the following resonance structures:

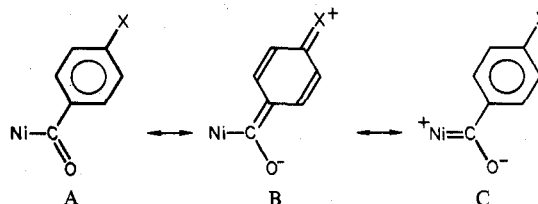


Table I. Spectral Data for *trans*-C₆Cl₅Ni(PPhMe₂)₂C(O)C₆H₄X-*p* (**2**) and *trans*-C₆Cl₅Ni(PPhMe₂)₂C₆H₄X-*p* (**1**)

complexes	IR spectra, ^a cm ⁻¹	¹ H NMR spectra, ^{b,c} δ							electronic spectra ^b	
		no.	X	Nujol	CH ₂ Cl ₂	temp ^d	P-CH ₃ (<i>J_P</i>) ^e	X, CH ₃		meta-H ₂ (<i>J_H</i>) ^e
2a	N(CH ₃) ₂	1528 (1556)m (1597)s	1540 (1562)m (1600)s	23	1.25, 1.29 dt (8)	2.95 s	6.53 d (9)	7.86 br	6.9-7.2	340 (29 400)
2b	OCH ₃	(1550)s 1577m (1599)s	(1560)m 1582m (1601)s	-40	1.24, 1.31 dt (8)	3.01 s	6.51 br	8.64 br, d (9)	6.8-7.3	332 (30 100)
2c	CH ₃	(1560)s 1577s (1602)m	(1560)s 1579s (1604)m	23	1.28, 1.29 dt (8)	3.77 s	6.69 d (8)	7.87 d (8)	6.9-7.2	330 (30 300)
1a	N(CH ₃) ₂			-40	1.28 br, s	3.78 s	6.69 d (8)	8.55 br	6.8-7.3	
1b^h	OCH ₃			23	1.27 t (8)	2.31 s	.. ^f	7.82 d (8)	6.9-7.2	330 (30 300)
1c^h	CH ₃			23	1.27 t (8)	2.32 s	.. ^f	.. ^g	6.8-7.3	
1f	N(CH ₃) ₃ ⁺			23	1.21 t (8)	2.76 s	6.43 d (8)	6.92 d (8)	7.0-7.3	382 (26 200)
				23	1.19 t (7)	3.63 s	6.43 d (8)	6.92 d (8)	7.0-7.2	365 (27 400)
				23	1.19 t (7)	2.14 s	6.63 d (8)	7.00 d (8)	7.0-7.2	365 (27 400)
				23	1.25 t (8)	3.48 s	6.83 d (9)	.. ^f	6.9-7.3	358 (27 900)

^a See the manuscript for the assignment of ν(CO) vibrations. ^b CH₂Cl₂ solution. ^c Abbreviations: s, singlet; d, doublet; t, triplet; dt, double triplets; br, broad. ^d In °C. ^e In Hz. ^f Overlapped with P-C₆H₅ proton resonances. ^g Very broad, and weak. ^h Some data have been reported elsewhere, ref 2.

Table II. Spectral Data for *trans*-[C₆Cl₅Ni(PPhMe₂)₂{C(OCH₃)C₆H₄X-*p*}]ClO₄ (**4**)

complexes	IR spectra, ^a cm ⁻¹	¹ H NMR spectra, ^{b,c} δ							
		no.	X	ν(COC)	ν(ClO ₄ ⁻)	temp ^d	P-CH ₃ (<i>J_P</i>) ^e	X, CH ₃	OCH ₃
4a	N(CH ₃) ₂	1180 vs	1090 vs	-40	1.28, 1.53 dt (8)	3.27 s	4.10 s	6.6-7.6 m	8.88 dd (9, 2)
				23	1.32, 1.52 dt (8)	3.26 s	4.36 s	6.4-7.6 m	8.89 dd (9, 2)
				50	1.31, 1.51 dt (8)	3.27 s	4.31 s	6.5-7.6 m	8.89 br, d (9)
				82	1.31, 1.50 dt (8)	3.26 s	4.45 s	6.5-7.6 m	8.9 br, s
4b	OCH ₃	1168 vs	1090 vs	-40	1.31, 1.53 dt (8)	4.02 s	4.33 s	6.8-7.7 m	9.14 dd (9, 2)
				23	1.38, 1.54 dt (8)	4.02 s	4.62 s	6.8-7.7 m	9.21 dd (9, 2)
				48	1.34, 1.51 dt (8)	4.02 s	4.56 s	6.8-7.7 m	9.16 br, s
				82	1.36, 1.51 dt (8)	4.03 s	4.72 s	6.8-7.6 m	.. ^f
4c	CH ₃	1180 s	1090 vs	-40	1.32, 1.53 dt (8)	2.56 s	4.43 s	6.8-7.7 m	9.08 d (8)
				23	1.37, 1.53 dt (8)	2.56 s	4.71 s	6.8-7.7 m	9.10 br
				82	1.38, 1.52 dt (8)	2.55 s	4.80 s	6.7-7.5 m	8.28 br

^a In Nujol. ^b In CH₂Cl₂ below 23 °C, and in CHCl₂CHCl₂ above 48 °C. ^c Abbreviations: s, singlet; d, doublet; t, triplet; dd, double doublets; dt, double triplets; m, multiplet; br, broad. ^d In °C. ^e In Hz. ^f The signal broadens to disappear above 70 °C.

A particularly low ν(CO) value has been reported for some neutral acyl complexes, Ru(PPh₃)(CO)(COR)Cl,¹⁴ Cp₂Zr-(COR)R,¹⁵ and CpFe(dppe)COPh,¹⁶ and unusual π-bonded acyl structures have been proposed.^{14,15} The contribution of resonance structures B and/or C in **2a-c** is supported by the following reaction on the carbonyl oxygen atom.

Methylation of Aroylnickel Intermediates. The reactions of aroylnickel intermediates with methyl fluorosulfonate were performed either with the isolated complexes or with the benzene solutions of complexes **1a-e** under carbon monoxide. The expected cationic aryl(methoxy)carbene complex could be obtained again in the three cases where the aryl group possessed an electron-donating para substituent. These complexes were purified and characterized in the form of perchlorate salts, **4a-c**. Again, the yield was the highest for **4a**. These results are indicative of the importance of resonance structure B (see above) in the aroylnickel complexes for the reaction. In the absence of carbon monoxide, **1a** was methylated at the dimethylamino group to give **1f** (X = N(CH₃)₃⁺-*p*).

All the carbene complexes thus prepared are crystalline with high thermal stability and are extremely inert toward moist air both in the solid state and in solutions. They are soluble in most polar solvents and haloalkanes without decomposition. The dichloromethane solutions at various concentrations gave molar conductance values within the range for a 1:1 electrolyte.¹⁷ The IR spectra (Table II) showed a characteristic very strong absorption at 1090 cm⁻¹ due to the free perchlorate anion. The spectra also showed a strong band at about 1180 cm⁻¹, which is tentatively assigned to the ν(COC) vibration. A value of 1240 cm⁻¹ has recently been reported¹⁶ for the vibration of [CpFe(dppe)C(OCH₃)C₆H₅]BF₄. The re-

activities of **4a-c** are under investigation, but the preliminary results indicate that **4a** is extremely inert toward a variety of nucleophiles including halides, amines, and even Grignard reagents.

¹H NMR Spectra. The ¹H NMR spectral data are summarized also in Table I for **2a-c**, together with those for **1a-c** and **1f**, and in Table II for **4a-c**.

The spectrum in the region of phosphine methyl proton resonances, δ 1.2-1.6, provides a good indication to establish the configuration of the complex.^{18a} The single 1:2:1 triplet pattern observed for **1a** is typical of a *trans* square-planar configuration. The spectrum of **2a** in dichloromethane exhibited, however, a 1:3:3:1 quartet and can be analyzed as the overlap of two 1:2:1 triplets. This indicates that the complex has a *trans* configuration.^{18b} The inequivalence of the methyl groups can be explained by a geometry in which the aryl group is either perpendicular to the plane of the molecule (rendering inequivalent the methyl groups on each phosphorus) or in the plane of the molecule (rendering inequivalent each of the PMe₂ groups). The former should display one ³¹P signal while the latter should display two ³¹P signals. We have measured ³¹P NMR and observed *only one* ³¹P resonance for both series of complexes **2a-c** and **4a-c**. This, however, does not unambiguously settle this point, because there is still a possibility of coincidental overlap of two resonances—the chemical shift changes were quite small among each three complexes. We can exclude the planar geometry of complex **2a** on steric grounds and that there is no electronic driving force in favor of that geometry (see comments below). Furthermore, if the two *trans* tertiary phosphines were nonequivalent, the ¹H NMR spectra would show two doublets, perturbed doublets, or perturbed triplets.¹⁹ Although none of

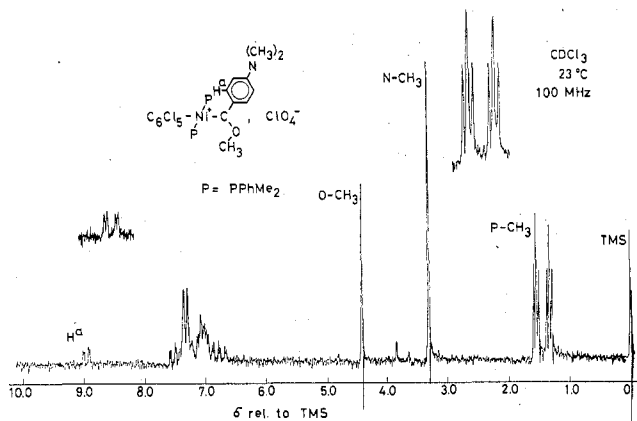


Figure 1. ^1H NMR spectrum of $\text{trans}-[\text{C}_6\text{Cl}_5\text{Ni}(\text{PPhMe}_2)_2]\text{C}(\text{OCH}_3)\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2\text{p}]\text{ClO}_4$ (**4a**) in deuteriochloroform.

these reasons is decisive, these are all in favor of perpendicular geometry of the aryl group. The spectrum of **2b** in dichloromethane or in benzene showed also two triplets, but with very little separation. On the other hand those of **2c** in several solvents showed exclusively a single triplet even at low temperatures. Accordingly, it seems that there is a rotational freedom of the aryl group in **2c** about the nickel-carbon bond, but there is still a possibility of its perpendicular orientation, if the spectral observation was a coincidental overlap of two triplets.

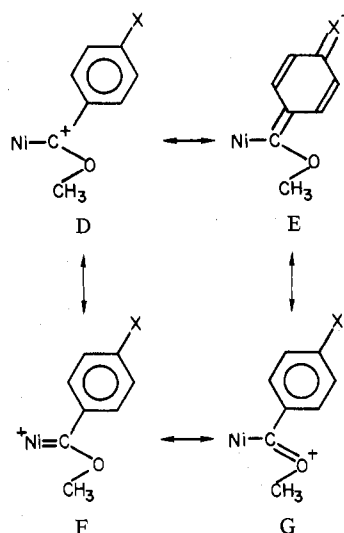
Two possible origins for the perpendicular orientation of aryl groups can be considered. The first is the presence of partial $d\pi-p\pi$ bond character between the nickel and the aryl carbon atoms, as represented in resonance structure C. This influence, however, is excluded because of the cylindrical distribution of nickel d_π orbitals. This would produce, probably, a very small rotational barrier, if any. The second is a steric hindrance by the two *cis* phosphine ligands, which is more plausible at present.

Aroyl ring protons of **2a-c**, in general, exhibit their resonances at both sides of those of the phosphine phenyl protons. The one at lower magnetic field is a broad singlet (**2a**) or a doublet (**2b** and **2c**) and can be assigned to the ortho protons. The equivalence of these two ortho protons, as well as two meta, may be explained as that there is a free rotation of the aryl group about the $\text{C}(\text{O})$ -aryl bond. At low temperatures, these ortho proton resonances shift to lower magnetic field.

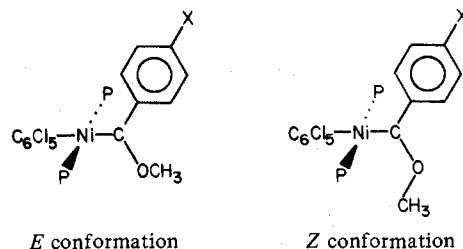
The aryl para substituents show their methyl proton resonances at lower magnetic field than those of the parent complexes, **1a-c**. These observations are also in accord with the effect of resonance B in **2a-c**.

The spectra of all the cationic carbene complexes **4a-c** exhibit two well-formed triplets for the phosphine methyl protons over the temperature range investigated, -40 to $+82$ $^\circ\text{C}$. A representative spectrum is shown in Figure 1. Characteristic of the spectrum is the observation of two doublets at such a low magnetic field region as δ 8.95, with a total intensity corresponding to ca. one proton. The resonance can be assigned to one of the four ring protons of the (dimethylamino)phenyl group, which is magnetically coupled with two of the other three ring protons. The nonequivalence of one ring proton is indicative of the fact that the aryl group is oriented coplanarly with the plane defined by the carbene carbon atom and its attached atoms, which is perpendicular to the nickel coordination plane. A proton situated directly over and close to the nickel coordination plane is well-known to exhibit its resonance at considerably lower magnetic field.^{20,21} Analogous low magnetic field resonance can be observed in the spectra of **4b** and **4c** (Table II). At elevated temperature these resonances broaden considerably, and narrow slightly at low temperatures.

Scheme II



The carbene methoxy proton resonance of **4a-c** is a very sharp singlet. This indicates the presence of only one isomer and is in contrast with the presence of two isomers²² in $\text{trans}-[\text{C}_6\text{Cl}_5\text{Ni}(\text{PPhMe}_2)_2]\text{C}(\text{OCH}_3)\text{CH}_3]\text{ClO}_4$. The *E* conformation shown below is sterically less favorable due to the presence of carbene aryl group, and the *Z* conformation



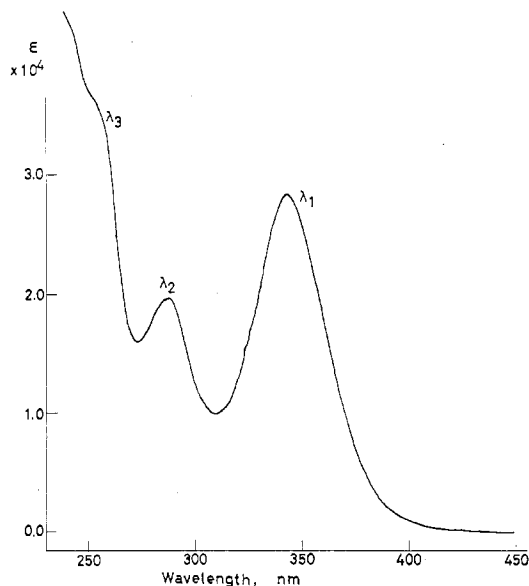
can be suggested for these aryl(methoxy)carbene complexes. The nickel atom in the *Z* conformation is seen to be protected sterically from the attack of nucleophiles. The carbene carbon atom, which is another reaction center considered, is also protected by the two phosphine ligands. These explain partially the unique inertness of **4a-c**. The conformation is in contrast with that found for Fischer's complexes, in which the aryl plane is perpendicular to the carbene plane at least in the solid state²³ and the methoxy group is rotating freely about the carbene carbon-oxygen bond in solution at room temperature.²⁴

The electronic configuration of our cationic aryl(methoxy)carbene complexes might be represented by the resonance scheme shown in Scheme II. The coplanarity of carbene aryl group with carbene plane must partly be attributed to the resonance E. Evidence for the resonance E is also seen in the proton chemical shifts of the aryl para substituents. Namely, in the three series of complexes, **1a-c**, **2a-c**, and **4a-c**, the carbene complexes show the resonance at the lowest magnetic field. The shift trend of carbene methoxy protons is in the order **4c** < **4b** < **4a**, which is explained by the increase in the contribution of resonance E in the order or by the decrease of resonance G.

Electronic Spectra. We have previously reported²⁵ the electronic spectra of a variety of pentachlorophenylnickel derivatives of types $\text{trans}-\text{C}_6\text{Cl}_5\text{Ni}(\text{PPhMe}_2)_2\text{X}$ and $\text{trans}-[\text{C}_6\text{Cl}_5\text{Ni}(\text{PPhMe}_2)_2\text{L}]\text{ClO}_4$. These complexes show a weak transition band in the region of 340–440 nm, which is attributable to the transition from the highest filled (d_{xy}) orbital to the lowest unfilled (σ^* , predominantly $d_{z^2-y^2}$). This so-called $d-d$ transition band is thought to be one of the useful tools for the identification of complex formation and is worth investigating for the present complexes.

Table III. Electronic Spectral Data^a for *trans*-[C₆Cl₅Ni(PPhMe₂)₂{C(OCH₃)C₆H₄-*p*}]ClO₄ (**4a-c**)

complexes	λ_{\max}		(log ϵ_{\max})	
	nm	cm ⁻¹		
4a	420	23 800	(4.75)	λ_1
	295	33 900	(sh)	λ_2
	255	39 200	(sh)	λ_3
4b	344	29 100	(4.45)	λ_1
	289	34 600	(4.29)	λ_2
	255	39 200	(sh)	λ_3
4c	324	30 900	(4.26)	λ_1
	284	35 200	(4.46)	λ_2
	255	39 200	(sh)	λ_3

^a CH₂Cl₂ solution.**Figure 2.** Electronic spectrum of *trans*-[C₆Cl₅Ni(PPhMe₂)₂C(OCH₃)C₆H₄OCH₃-*p*]ClO₄ (**4b**) in dichloromethane.

The two series of complexes, **1a-c**, **f** and **2a-c**, show the band as a weak shoulder due to the presence of a very intense band in the ultraviolet region tailing toward the visible region; the spectral data are included in Table I. It is seen from the table that the aryl complexes show the band at a considerably higher energy region than aryl complexes and that the more electron donating para substituent in both series of complexes causes the band to shift to a lower energy region. These results are quite consistent with the presence of a stronger $d\pi-\pi$ bond in the nickel-aryl bond of **2a-c** than in the nickel-aryl bond of **1a-c** and provide good evidence for the cooperation of resonances B and C in **2a-c**. It is noteworthy here that these aryl groups take precedence in the spectrochemical series over cyanide or carbon monoxide.²⁵

Unfortunately the weak, $d-d$ transition band of carbene complexes **4a-c** could not be detected in their electronic spectra because of the presence of very intense bands in the region. The spectral data of these bands are summarized in Table III, and the representative spectrum is shown in Figure 2. The λ_{\max} of the lowest energy band, λ_1 , is quite sensitive to the change of the aryl para substituent, and blue shifts of 5300 and 7100 cm⁻¹ were observed in going from **4a** to **4b** and **4c**, respectively. The λ_{\max} of the second band, λ_2 , is less sensitive to the change of the para substituent, but the intensity increases in the reverse order found for λ_1 . The third band observed at 255 nm is of shoulder character and is observed in all the spectra of **4a-c** at the same wavelength.

The two intense bands, λ_1 and λ_2 , are characteristic of the present aryl(methoxy)carbene complexes, and no such intense band could be observed in the electronic spectra of methyl-

Table IV. Analytical Data for New Compounds

compd	% C		% H		% N	
	calcd	found	calcd	found	calcd	found
1a	51.15	51.14	4.58	4.51	1.99	2.05
1f	45.46	45.44	4.31	4.45	1.71	1.77
2a	50.83	50.67	4.40	4.32	1.91	1.92
2b	50.08	50.04	4.06	4.17		
2c	51.22	50.80	4.16	4.19		
3a	45.32	45.17	2.54	2.51	3.52	3.61
4a	45.38	45.09	4.17	3.95	1.65	1.61
4b	44.64	44.65	3.87	3.84		
4c	45.52	45.28	3.94	3.75		
5a	45.51	45.25	2.73	2.66	3.79	3.69

(alkoxy)carbene complexes, *trans*-[C₆Cl₅Ni(PPhMe₂)₂C(OR)CH₃]ClO₄, in which the expected $d-d$ transition was observed in the region of 330–335 nm.²⁶ Although a firm assignment of λ_1 and λ_2 is not possible at this time, the facts shown above seem to indicate that the two bands are charge transfer in nature.

Experimental Section

Analytical data for new compounds are summarized in Table IV. IR spectra were recorded on a Hitachi 225 spectrophotometer over the range 4000–500 cm⁻¹. ¹H NMR spectra were recorded on a JEOL Model JNM-PS-100 spectrometer operating at 100 MHz. Chemical shifts were measured relative to Me₄Si as an internal standard. Electronic spectra were measured on a Hitachi Model 200-20 spectrophotometer.

Preparation of *trans*-Aryl(pentachlorophenyl)bis(phenyldimethylphosphine)nickel(II) Complexes (1a-e). *trans*-C₆Cl₅Ni(PPhMe₂)₂C₆H₄N(CH₃)₂-*p* (**1a**). An ethereal solution of *p*-(dimethylamino)phenyllithium was prepared from *p*-bromo-*N,N*-dimethylaniline (2.2 g, 11 mmol) and a 15% *n*-pentane solution of *n*-butyllithium (6.4 mL, 10 mmol) in 25 mL of dry diethyl ether. The two reagents were mixed at 0 °C under a nitrogen atmosphere, and the solution was stirred at room temperature for 1 h. The *p*-(dimethylamino)phenyllithium solution was cooled on an ice bath, and a dry benzene (15 mL) solution of *trans*-C₆Cl₅Ni(PPhMe₂)₂Cl (3.1 g, 5 mmol) was added. The mixture was stirred for 1 h at 0 °C and then 1 h at room temperature. It was washed with cold water containing NH₄Cl, and the solvents of the organic layer were removed under a reduced pressure. The residue was recrystallized from acetone-methanol to give yellow-orange crystals of **1a**: yield 54%; mp 164–165 °C.

The other complexes, **1b-e**, were prepared as previously reported.²

Isolation of Arylnickel(II) Intermediates, 2a-c. *trans*-C₆Cl₅Ni(PPhMe₂)₂C(O)C₆H₄N(CH₃)₂-*p* (**2a**). A solution of **1a** (705 mg, 1 mmol) in 80 mL of acetone was stirred at 0 °C for 45 min under carbon monoxide at atmospheric pressure. The resultant precipitate was filtered under air while cold to give **2a** (485 mg, mp 109 °C dec). The filtrate was concentrated to ca. one-fourth volume under a reduced pressure to give an additional precipitate of **2a** (85 mg, mp 108 °C dec) with a total yield of 78%. The analytical sample was obtained by recrystallization from cold acetone-methanol; mp 115 °C dec (evacuated capillary).

trans-C₆Cl₅Ni(PPhMe₂)₂C(O)C₆H₄OCH₃-*p* (**2b**). A solution of **1b** (692 mg, 1 mmol) in 30 mL of dichloromethane was stirred at 20 °C for 2 h under carbon monoxide. *n*-Hexane (100 mL) was added and the solution was condensed to ca. one-third volume under reduced pressure. The resultant precipitate was filtered quickly under air. For the purification it was dissolved in acetone (3 mL/100 mg) at room temperature under nitrogen, followed by filtration if turbid. A quantity of methanol equal to twice the volume of the solution was added, and the solution was cooled for 1 week in a refrigerator to give orange-yellow crystals of **2b**: yield 31–47%; mp 109 °C dec (evacuated capillary).

trans-C₆Cl₅Ni(PPhMe₂)₂C(O)C₆H₄CH₃-*p* (**2c**). In a method similar to that used above for **2b**, **1c** was reacted with carbon monoxide for 2.5 h in dichloromethane. The crude **2c** was purified from acetone-methanol: yield 15–40%; mp 111 °C dec (evacuated capillary).

Reaction of 2a with Carbon Monoxide. A solution of **1a** (211 mg, 0.3 mmol) in 30 mL of acetone was stirred at room temperature under carbon monoxide to give a yellow precipitate of **2a**. The mixture was stirred further for 24 h to dissolve the precipitate. The carbon

monoxide atmosphere was replaced by air, and the solution was stirred at room temperature again for 24 h to oxidize the nickel(0) species expected to be formed.² The solvent was then evaporated under a reduced pressure, and the residue was treated with diethyl ether-water. The ether layer was separated and then evaporated to leave a white solid, which was recrystallized from ethanol to give $C_6Cl_5(O)-C_6H_4N(CH_3)_2-p$ (**3a**): yield 55% based on **1a**; mp 182–184 °C; ¹H NMR (CH_2Cl_2) 3.00 singlet and 3.06 singlet ($N(CH_3)_2$), 6.5–7.7 multiplet (C_6H_4).

Analogous reactions for **2b** and **2c** have been reported previously.²

Preparation of Cationic Aryl(methoxy)carbene Complexes, 4a–c. *trans*- $[C_6Cl_5Ni(PPhMe_2)_2\{C(OCH_3)C_6H_4N(CH_3)_2-p\}][ClO_4]$ (**4a**). **Method I.** To a solution of **2a** (733 mg, 1 mmol) in 20 mL of dichloromethane was added 0.2 mL of CH_3OSO_2F under an atmosphere of nitrogen. The mixture was stirred at room temperature for 2 h. It was diluted by addition of 40 mL of dichloromethane and washed with water to remove the unreacted CH_3OSO_2F . The dichloromethane layer was separated, and the solvent was removed under a reduced pressure. The resultant sticky solid was dissolved in methanol (ca. 70 mL) under air. To the clear solution was added NH_4ClO_4 (141 mg, 1.2 mmol), and the mixture was stirred vigorously for 0.5 h at room temperature and then 0.5 h at 0 °C to give an orange-yellow precipitate of **4a**: yield 73%; mp 206 °C dec. The analytical sample was obtained by recrystallization from methanol, mp 212 °C dec.

Method II. A solution of **1a** (439 mg, 0.7 mmol) in 10 mL of dry benzene was placed under an atmosphere of carbon monoxide. The solution was stirred at room temperature for 0.5 h. Then 0.2 mL of CH_3OSO_2F was added, and the mixture was further stirred for 1 h. The resulting yellow precipitate was separated by filtration or by decantation under air, washed with water, and dissolved in methanol. The methanol solution was treated similarly as above with NH_4ClO_4 to give the precipitate of **4a**; yield 72%. The molar conductivities of 1.0×10^{-2} , 10^{-3} , and 10^{-4} M solutions in dichloromethane at 25 °C were 32.0, 49.3, and $76.7 \Omega^{-1} cm^2 M^{-1}$, respectively.

trans- $[C_6Cl_5Ni(PPhMe_2)_2\{C(OCH_3)C_6H_4OCH_3-p\}][ClO_4]$ (**4b**). **Method I.** In an analogous manner to the preparation of **4a**, a reaction of **2b** (216 mg, 0.3 mmol) and CH_3OSO_2F (0.3 mL) in 7 mL of dichloromethane gave **4b**: yield 50%; mp 203 °C dec.

Method II. A solution of **1b** (691 mg, 1 mmol) and CH_3OSO_2F (0.2 mL) in 10 mL of dry benzene was stirred at room temperature under carbon monoxide for 2 h. The resulting precipitate was treated in an analogous manner to the preparation of **4a** (method II); yield of **4b** 41%. The molar conductivities of 1.0×10^{-2} , 10^{-3} , and 10^{-4} M solutions in dichloromethane at 25 °C were 29.0, 47.6, and $78.4 \Omega^{-1} cm^2 M^{-1}$, respectively.

trans- $[C_6Cl_5Ni(PPhMe_2)_2\{C(OCH_3)C_6H_4CH_3-p\}][ClO_4]$ (**4c**). A solution of **1c** (676 mg, 1 mmol) and CH_3OSO_2F (0.2 mL) in 20 mL of dry benzene was stirred at room temperature under carbon monoxide for 3 h. The resulting precipitate was treated in an analogous manner to the preparation of **4a** (method II); yield of **4c** 28%; mp 179–180 °C dec. The molar conductivities of 1.0×10^{-2} , 10^{-3} , and 10^{-4} M solutions in dichloromethane at 25 °C were 29.7, 48.1, and $78.9 \Omega^{-1} cm^2 M^{-1}$, respectively.

Reaction of 1a with Methyl Fluorosulfate. To a solution of **1a** (352 mg, 0.5 mmol) in 5 mL of dichloromethane was added 0.15 mL of CH_3OSO_2F under an atmosphere of nitrogen. The mixture was stirred for 1 h at room temperature. It was diluted by addition of 10 mL of dichloromethane and washed with water. The solvent was removed

under a reduced pressure, and the residue was dissolved in methanol. To the clear solution was added NH_4ClO_4 (100 mg, an excess), and the mixture was stirred vigorously for 15 min to give yellow precipitate of *trans*- $C_6Cl_5Ni(PPhMe_2)_2C_6H_4N(CH_3)_3^+-p, ClO_4^-$ (**1f**): yield 71%; mp 216 °C dec.

Thermal Decomposition of 2a in Tetrachloroethylene. A solution of **2a** (220 mg, 0.3 mmol) in 5 mL of tetrachloroethylene was heated on a boiling water bath for 1 h under air. A small amount of dark brown precipitate was filtered off, and the solvent was removed under a reduced pressure. The residue was extracted with 4 mL of dichloromethane, and the extract was chromatographed on a 15-cm column of Florisil utilizing dichloromethane as the eluent. A colorless to light yellow fraction and a yellow-brown fraction were collected separately. The solvent was removed and each residue was recrystallized from ethanol to give colorless crystals of $C_6Cl_5C_6H_4N(CH_3)_2-p$ (**5a**) from the former fraction (yield 51%; mp 210–211 °C) and orange-brown crystals of *trans*- $(CCl_2=CCl)Ni(PPhMe_2)_2Cl$ from the latter fraction (yield 39%; mp 123 °C, lit.² 123 °C). ¹H NMR of **5a** (CH_2Cl_2) 3.00 singlet ($N(CH_3)_2$), 6.77 doublet and 7.06 doublet ($J_H = 9$ Hz) (C_6H_4).

Registry No. **1a**, 66809-26-5; **1b**, 60949-84-0; **1c**, 60949-82-8; **1f**, 66809-28-7; **2a**, 66809-19-6; **2b**, 66809-29-8; **2c**, 66809-20-9; **3a**, 66809-30-1; **4a**, 66809-22-1; **4b**, 66809-24-3; **4c**, 66809-25-4; **5a**, 66809-31-2; *trans*- $C_6Cl_5Ni(PPhMe_2)_2Cl$, 15526-04-2.

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