Chemistry of Alkoxycarbonyl, Acyl, and Alkyl Compounds of Nickel(II) and Palladium(II)

Sei Otsuka,* Akira Nakamura, Toshikatsu Yoshida, Masanobu Naruto, and Kikuo Ataka

Contribution from the Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka, Japan. *Received October 20, 1972*

Abstract: Oxidative addition leading to alkoxycarbonyl, acyl, and alkylnickel(II) and palladium(II) compounds was studied. Optically active ethyl α-bromopropionate or ethyl bromophenylacetate adds to $Pd(t\text{-}BuNC)_2$ with loss of stereochemical integrity at the carbon atom. Some alkoxycarbonyl and acylnickel(II) isocyanide compounds formed *in situ* undergo ready decarboxylation or decarbonylation accompanied by alkyl migration. The alkoxycarbonyl carbon–metal and acyl carbon–metal bondings are discussed in relation to thermal stability; the interpretation accommodates the enhanced propensity of organonickel(II) compounds for elimination reactions. Thermal decomposition of complexes of type $MX(R)L_2$ was studied by tracing the fates of organic as well as of metal moieties to establish the relationship between one structure of the alkyl moiety and the fragmentation mode. The thermolysis has proved a convenient route to the univalent metal complexes. Insertion reactions, *e.g.*, olefin insertion into an alkoxycarbonyl–palladium bond, are described with emphasis being placed on the aspect bearing on palladium-catalyzed olefin substitution reactions.

Organic syntheses with transition metal compounds are the subject of much current interest. Particularly, group VIII transition metal complexes have been shown to catalyze various olefin reactions such as oligomerization, isomerization, or substitution in which a σ-organo–transition metal species plays an important role. However, with the isolation being generally difficult, only scattered information is available on the genuine σ-organonickel[1a,b] or palladium species.[2] In connection with our work on isocyanide insertion reactions of organonickel and palladium compounds,[3] we have undertaken a systematic study on the reactivity of alkyl, acyl, and alkoxycarbonylmetal compounds.[4] In this paper we are concerned with (1) oxidative addition of various organic halides to zerovalent nickel and palladium compounds, (2) carbon dioxide or carbon monoxide elimination from the alkoxycarbonyl or acyl–metal complexes, (3) thermal decomposition of alkyl and arylmetal compounds, (4) reaction of σ-bonded organometallic compounds with olefins or like reagents, and (5) isolation of univalent nickel and palladium compounds.

Incentive for these studies was derived from several unexplored aspects of this field: (1) stereochemistry of an optically active alkyl halide addition to Ni(0) or Pd(0) compounds, (2) relative thermal stability of organonickel(II) and palladium(II) compounds and factors governing their stability, and (3) thermal decomposition patterns of alkyl, acyl, and alkoxycarbonyl compounds. We are also interested in finding uses for these organometallic compounds, in particular alkoxycarbonyl metals.

Results and Discussion

Oxidative Addition of Haloformate and Related Halides. Alkoxycarbonyl–transition metal compounds[5-8] are prepared by nucleophilic addition of alkoxide ion or even alcohol on cationic carbonyl compounds, by alcoholysis of carbamoyl derivatives, and by oxidative addition of haloformates. Despite this previous research the properties and reactivities of Ni–COOR and Pd–COOR bonds still remain to be explored. The additions of alkyl and aryl chloroformates are investigated for zerovalent d^{10} metal complexes ML_4 (M = Ni, Pd; L = t-BuNC, PPh_3, $P(OPh)_3$), $ML_2(C_2H_4)$ (M = Ni; L = PPh_3), and ML_2 (M = Pd; L = t-BuNC).

A. Nickel Compounds. The nickel phosphine complexes generally afford the expected alkoxycarbonyl compounds. Thus alkyl chloroformates react with $Ni(PPh_3)_4$ or $Ni(C_2H_4)(PPh_3)_2$ in toluene at room temperature producing thermally unstable, very air-sensitive yellow complexes of formula $NiCl(COOR)(PPh_3)_2$ as the main product. Tables I and II summarize their analytical data and properties. This is the first reported isolation of alkoxycarbonyl–nickel complexes. The yield for the benzyloxy complex (**1c**) is low (10–30%) due to thermal decomposition yielding carbon dioxide, 1,2-diphenylethane, and the known univalent nickel complex $NiX(PPh_3)_3$ (**4**, X = Cl; **5**, X = Br), which can be prepared from an alkyl halide and $Ni(PPh_3)_4$.[9,10] The decomposition products appear to suggest an intermediacy of $NiCl(CH_2C_6H_5)(PPh_3)_2$. Since the Ni–C(O)OR bond in $NiX(CO_2R)L_2$ is thermally more stable than the Ni–R bond in $NiX(R)L_2$ (dec <0° for R = $CH_2C_6H_5$; L = PPh_3), the intermediacy, we believe, is unlikely (Scheme I). This view receives some support from a similar reaction of nickel isocyanide compounds (*vide infra*). It is not, however,

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[1] (a) D. R. Fahey, *Organometal. Chem. Rev., Sect. A*, 7, 245 (1972); (b) P. Heimbach, P. W. Jolly, and G. Wilke, *Advan. Organometal. Chem.*, 8, 29 (1970).

[2] P. M. Maitlis, "The Organic Chemistry of Palladium," Vol. 1, Academic Press, New York, N. Y., 1971, pp 53–103.

[3] S. Otsuka, A. Nakamura, and T. Yoshida, *J. Amer. Chem. Soc.*, **91**, 7196 (1969).

[4] A preliminary note has been published: S. Otsuka, M. Naruto, T. Yoshida, and A. Nakamura, *J. Chem. Soc., Chem. Commun.*, 396 (1972).

[5] P. Fitton, M. P. Johnson, and J. E. McKeon, *Chem. Commun.*, 6 (1968).

[6] H. C. Clark, K. R. Dixon, and W. J. Jacobs, *J. Amer. Chem. Soc.*, **91**, 1346 (1969).

[7] S. D. Ibekwe and K. A. Taylor, *J. Chem. Soc. A*, 1 (1970), and references cited therein.

[8] L. Malatesta, M. Angoletta, and G. Caglio, *J. Chem. Soc. A*, 1836 (1970), and references cited therein.

[9] P. Heimbach, *Angew. Chem., Int. Ed. Engl.*, 3, 648 (1964).

[10] L. Porri, M. C. Gallazzi, and G. Vitulli, *Chem. Commun.*, 228 (1967).

Table I. Properties and Analytical Data of $MCl(CO_2R)L_2$

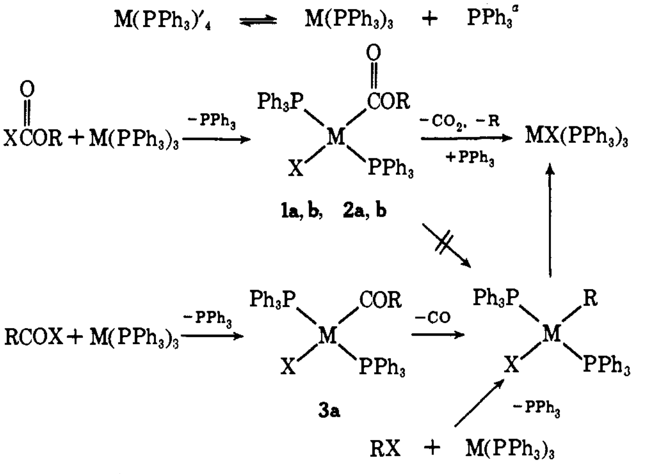
No.	Compound	Color	Mp, °C	Found, % C	Found, % H	Found, % N	Calcd, % C	Calcd, % H	Calcd, % N
1a	$NiCl(CO_2CH_3)(PPh_3)_2$	Yellow	150–153 dec	67.30	4.89		67.33	4.92	
1b	$NiCl(CO_2C_2H_5)(PPh_3)_2$	Yellow	134–138 dec	65.01	4.92		67.71	5.10	
2a	$PdCl(CO_2CH_3)(PPh_3)_2$	Colorless	190–192 dec	64.08	4.86		62.91	4.59	
2b	$PdCl(CO_2C_2H_5)(PPh_3)_2$	Colorless	170–190 dec	63.65	4.70		63.34	4.77	
2c	$PdCl(CO_2C_2H_5)[P(OPh)_3]_2$	Colorless	128–136 dec	55.92	4.21		54.63	4.22	
2d	$PdCl(CO_2CH_3)(t\text{-}BuNC)_2$	Colorless	106–108	39.55	5.80	7.72	39.25	5.78	7.63
2e	$PdCl(CO_2C_2H_5)(t\text{-}BuNC)_2$	Colorless	98–100	41.38	6.17	7.36	40.95	6.09	7.35
2f	$PdCl(CO_2CH_2C_6H_5)(t\text{-}BuNC)_2$	Pale yellow	137–139	49.03	5.68	6.30	48.76	5.70	6.32

Table II. Spectral Data of $MCl(CO_2R)L_2$

	Ir, cm$^{-1\,a}$			Nmr, τ^b			
Compound	$\nu_{C\equiv N}$	$\nu_{C=O}$	ν_{M-Cl}	t-Bu	CH_3	CH_2	Ph
1a		1629 s 1649 s	380 m		7.48 (s)		1.9 (m) 2.9 (m)
1b		1630 s	386 m				
1c[c]		1630 s					
2a		1656 m 1672 s	328 m		7.57 (s)		2.3 (m) 2.6 (m)
2b		1645 s 1633 s	335 m				
2c		1670 s	332 m		8.97 (t) $J = 7$ Hz	6.03 (q)	
2d	2205 s	1680 s		9.25 (s)	6.35 (s)		
2e	2210 s	1670 s		9.24 (s)	8.86 (t) $J = 7$ Hz	5.22 (q)	
2f	2215 s	1675 s		9.33 (s)		4.68 (s)	2.8 (m)

[a] Nujol mull. [b] In C_6D_6 for **2d**, **2e**, and **2f** and in $CDCl_3$ for the rest. TMS as internal reference. Multiplicity is indicated in parentheses. [c] **1c** = $NiCl(CO_2CH_2C_6H_5)(PPh_3)_2$.

Scheme I



[a] C. A. Tolman, W. C. Seidl, and D. H. Gerlach, *J. Amer. Chem. Soc.*, **94**, 2669 (1972).

possible to exclude the possibility of its existence as a transient species.

The stable complex $Ni[P(OC_6H_5)_3]_4$ does not react with alkyl chloroformates.

Oxidative addition of acyl or aroyl halides[11-13] and decarbonylation (or alkyl migration reactions) of the adduct[14,15] are well known. However, virtually no information is available for acylnickel compounds. Carbon monoxide insertions into transient carbon-nickel bonds are postulated in various catalytic reactions.[16-18] Yet, isolation of acylnickel compounds by carbonylation of α-alkylnickel has never been successful.

Acetyl chloride reacts readily with $Ni(C_2H_4)(PPh_3)_2$ or $Ni(PPh_3)_4$ in toluene at room temperature; the products isolated are $NiCl(PPh_3)_3$ and carbonyl complexes, $Ni(CO)_2(PPh_3)_2$ and $Ni(CO)_3(PPh_3)$. In addition, ethane is detected by glpc. Similar reaction of acetyl iodide with $Ni(C_2H_4)(PPh_3)_2$ produces unexpectedly *trans*-$NiI_2(PPh_3)_2$ only, no Ni(I) complex being detected. When benzoyl chloride is allowed to react with $Ni(PPh_3)_4$ at low temperature (0°), the yellow phenylnickel complex *trans*-$NiCl(C_6H_5)(PPh_3)_2$[19,20] is isolated (90%) together with a small amount of a mixture of carbonylphosphine–nickel complexes. The phenyl-

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(11) (a) J. P. Collmann, *Accounts Chem. Res.*, **1**, 136 (1968); (b) J. P. Collmann and W. R. Roper, *Advan. Organometal. Chem.*, **7**, 53 (1968).

(12) J. P. Collmann and C. T. Sears, Jr., *Inorg. Chem.*, **7**, 27 (1968); (b) J. P. Collmann, N. W. Hoffman, and D. E. Morris, *J. Amer. Chem. Soc.*, **91**, 5661 (1969).

(13) M. Kubota and D. M. Blake, *J. Amer. Chem. Soc.*, **93**, 1368 (1971), and references cited therein.

(14) J. Tsuji and K. Ohno, *Synthesis*, 157 (1967).

(15) J. Blum, S. Kraus, and Y. Pickholz, *J. Organometal. Chem.*, **33**, 227 (1971).

(16) G. W. Parshall and J. J. Mrowca, *Advan. Organometal. Chem.*, **7**, 157 (1968).

(17) G. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds," Vol. 2, Methuen, London, 1968, pp 203–287.

(18) G. P. Chiusoli and L. Cassar, *Angew. Chem., Int. Ed. Engl.*, **6**, 124 (1967).

(19) K. P. MacKinnon and B. O. West, *Aust. J. Chem.*, **21**, 2801 (1968).

(20) M. Hidai, T. Kashiwagi, T. Ikeuchi, and Y. Uchida, *J. Organometal. Chem.*, **30**, 279 (1971).

Table III. Properties and Analytical Data of Polyimino–Nickel Complexes

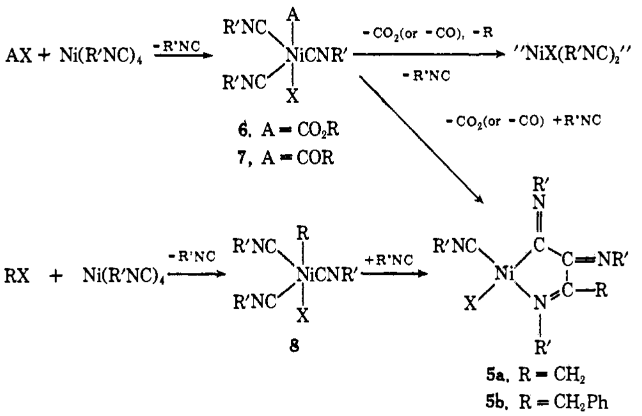
				Found				Calcd			
No.	Compound[b]	Color	Mp, °C	% C	% H	% N	Mol wt[a]	% C	% H	% N	Mol wt
5a	$NiCl[(t\text{-}BuN{=}C)_3CH_3]L$	Orange	125–130 dec	57.28	8.70	13.18	478	57.09	8.92	12.68	442
5b	$NiCl[(t\text{-}BuN{=}C)_3CH_2C_6H_5]L$	Orange	92–94 dec	63.21	8.21	10.69	469	62.61	8.39	10.82	518
5c	$NiCl[(t\text{-}BuN{=}C)_4COCH_3]L$	Orange	75–120 dec	58.66	8.75	12.67	580	58.31	8.90	12.48	553
5d	$NiCl[(t\text{-}BuN{=}C)_5COC_6H_5]L$	Yellow	83–85	63.80	8.46	11.58	676	63.66	8.52	12.03	696
5e	$NiI[(t\text{-}BuN{=}C)_3C_2H_5]L$	Red	90.5–91	48.25	7.68	10.30	572	48.29	7.55	10.23	548
5f	$NiI[(t\text{-}BuN{=}C)_3\text{-}n\text{-}C_3H_7]L$	Red	89–89.5	49.20	7.75	10.01	495	49.22	7.72	9.97	562
5g	$NiI[(t\text{-}BuN{=}C)_3\text{-}i\text{-}C_3H_7]L$	Reddish brown	76–78	48.82	7.72	9.82	530	49.22	7.72	9.97	562

[a] Vapor pressure osmometry in benzene. [b] L = t-BuNC.

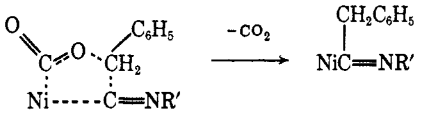
nickel compound can be prepared by oxidative addition of the corresponding phenyl halide.[1] The marked tendency to eliminate CO from the Ni–C(O)R bond contrasts the stability of the Pd–C(O)R bond and will be discussed later. It may be noted here that carbonylation of the $Ni–C_6H_5$ bond in $NiCl(C_6H_5)L_2$ (L = tris(bornyl)phosphite) is possible affording the stable benzoyl compound $NiCl(COC_6H_5)L_2$.[21] The dehalogenocarbonylation of acyl halides with low-valent nickel complexes, which can be effected at low temperature, may have a preparative significance.

The nickel isocyanide complexes behave differently from the phosphine complexes exhibiting a sophisticated chemistry. Alkyl chloroformates react with Ni(t-BuNC)$_4$ in benzene at ambient temperature yielding polyimino chelate complexes (**5a**, R = CH_3; **5b**, R = $C_6H_5CH_2$). The iodo analog of **5a** has been prepared with a better yield from methyl iodide and Ni(t-BuNC)$_4$[3] (Scheme II). Structural assignment of the polyimino compounds **5a,b** (Table III) is made by comparing their spectroscopic data with those of the similar compound obtained previously.[3] The complex **5b** shows a ^1H nmr spectrum of the AB spin system for the methylene protons (Table IV) which implies either a nonplanar structure around the tetracoordinated nickel atom or a restricted rotation of the benzyl group. The molecular model shows steric hindrance to rotation. Conclusion is deferred, however, until an X-ray analysis elucidates the molecular structure. The observation of two magnetically nonequivalent methyl groups of $PPhMe_2$ in similar iminoacyl–palladium(II) complexes was interpreted in terms of deviation from square-planar structure.[22]

Scheme II



A salient feature of the reaction of alkyl chloroformates with Ni(t-BuNC)$_4$ is the extensive decarboxylation as detected by glpc. The reaction of nickel phosphine complexes (*vide supra*) suggests that incipient formation of an alkoxycarbonyl complex **6** (A = C(O)OR) is likely, for which a pentacoordination may be postulated by analogy with the isolated acyl complex **7** (A = COC_6H_5). The migration of the benzyl group in **6** and the absence of an alkyl coupling product (1,2-diphenylethane) are best accommodated by a cyclic intermediate. A mechanism involving the $C_6H_5CH_2$–Ni species **8** seems unlikely since a σ-bonded alkyl group without β hydrogen gives the coupling product (see Table VI).



Ethyl chloroformate reacts slowly with Ni(t-BuNC)$_4$ in benzene at room temperature producing a small amount of dark colored ill-defined nickel compounds. The reaction carried out in boiling benzene yields a dark brown polymeric nickel compound of formula "NiCl(t-BuNC)$_2$." The poor solubility in common organic solvents and the instability in solution prevent study of its solution chemistry; *e.g.*, nmr measurement is hampered due to precipitation of paramagnetic substances. The ir (Nujol mull) absorption bands at 2200, 2180 ($\nu_{N\equiv C}$) and 1740 cm^{-1} ($\nu_{N=C}$) correspond to the terminal and bridging isocyanide groups, respectively, indicating a cluster structure. A more soluble bromo analog "NiBr(t-BuNC)$_2$" is obtained as light brown fine crystals from reaction of Ni(t-BuNC)$_4$ with $BrCH_2CO_2CH_3$. The ir spectrum also contains absorptions ascribable to the terminal (2200 cm^{-1}) and bridging NC stretchings (1700 cm^{-1}) and the ^1H nmr shows two nonequivalent *tert*-butyl proton resonances. Consequently the bromo compound is believed to also have a cluster structure involving bridging isocyanide ligands. Cryoscopic molecular weight measurements failed to illustrate a plausible size of the molecule due to dissociation of the isocyanide ligand.

Phenyl chloroformate with Ni(t-BuNC)$_4$ produces neither an insertion product nor an isolable phenoxy-

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(21) S. Otsuka, K. Tani, and I. Kato, to be submitted for publication.

(22) Y. Yamamoto and H. Yamazaki, *Bull. Chem. Soc. Jap.*, 43, 2653 (1970).

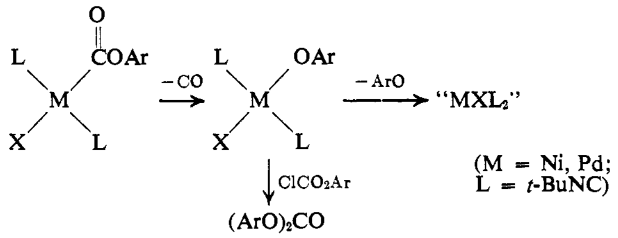
Table IV. Spectral Data of Polyimino–Nickel Complexes

Compound	Ir, cm$^{-1\,a}$				Nmr, τ^b				
	$\nu_{C\equiv N}$	$\nu_{C=N}$	ν_{CO}	ν_{Ni-Cl}	t-BuN≡C	t-BuN=C	CH_3	Ph	CH_2
5a	2180 s	1672		305 m	9.12 (3)	8.52 (3)	8.02 (1)		
		1643				8.42 (3)			
		1620				8.32 (3)			
5b	2185 s	1680		308 m	9.17 (9)	8.57 (9)		2.99 (5)	5.25^c (1)
		1620				8.46 (9)			6.33^c (1)
						8.35 (9)			
5c	2170 s	1645 m (br)	1705 m		9.15 (3)	8.80 (3)	7.73 (1)		
		1609 m (br)				8.53 (3)			
						8.31 (3)			
5d	2174 s	1645	1675		9.15 (1)	8.84 (1)			
		1638				8.55 (1)			
		1612				8.39 (1)			
		1598				8.29 (1)			
		1582				8.24 (1)			

[a] Nujol mull. [b] In C_6D_6 with TMS as internal reference. Intensity ratios are shown in parentheses. [c] Showed AB spin spectrum (J = 13 Hz).

carbonyl compound. When the phenyl ester is brought into contact with Ni(t-BuNC)$_4$ in solution at room temperature, decarbonylation takes place, instead of decarboxylation, producing diphenyl carbonate and a brown solid which contains "NiCl(t-BuNC)$_2$" as detected by the ir spectrum (Scheme III). The carbon monoxide in part is trapped as a zerovalent nickel complex Ni(CO)(t-BuNC)$_3$ produced in a small amount.

Scheme III



The reaction of Ni(t-BuNC)$_4$ with acyl halides follows essentially the same pattern as that with alkyl or alkoxycarbonyl halides. Alkylimino complexes **5a** and **5b** are produced from acetyl and phenylacetyl chloride, respectively, indicating decarbonylation. An acylimino compound **5c** (Table III and IV) is also found in the reaction of acetyl chloride. Since decarbonylation of **5c** does not take place under comparable conditions, decarbonylation of an acetylnickel compound **7** (A = $COCH_3$) leading to an alkylnickel species presumably precedes the isocyanide insertion, thus forming **5a** (Scheme II). The low yield of **5a** may be ascribed to the short life of the methylnickel species. As described previously,[3] benzoyl chloride adds to Ni(t-BuNC)$_4$ to form an unstable pentacoordinated nickel compound, **7**, without decarbonylation which gives rise *via* benzoyl group migration to a polyimino compound, NiCl[(t-BuNC)$_5$COC$_6$H$_5$]L (L = t-BuNC). A similar reaction pathway is postulated for the reaction with acyl halides or alkoxycarbonyl halides (Scheme II), although the two reactions may differ in detail regarding intervention of the alkylnickel species. An alkylnickel species could be involved in the formation of **5a**,**b**, since NiCl(Ar)(PPh$_3$)$_2$ was shown to be thermally more stable than NiCl(COAr)(PPh$_3$)$_2$.

In the reaction with Ni(0) complexes aryl chlorides add only sluggishly at moderate temperature. The neat decarbonylation reaction of aroyl compounds NiCl(COAr)L$_2$ provides an access to chloronickel compounds NiCl(Ar)L$_2$.

Because of the instability of alkylnickel compounds, the stereochemistry of the oxidative addition of alkyl halide to nickel compounds was not studied (see the next section).

B. Palladium Compounds. Oxidative addition of alkyl chloroformates to a palladium(0) compound has precedent, and formation of PdCl(CO$_2$C$_2$H$_5$)(PPh$_3$)$_2$ was reported by Fitton, *et al.*,[5] without details. The addition to Pd(PPh$_3$)$_4$, Pd[P(OC$_6$H$_5$)$_3$]$_4$, or "Pt(t-BuNC)$_2$" requires a higher temperature compared to the reaction with nickel compounds. Generally the expected alkoxycarbonyl complexes PdX(CO$_2$R)L$_2$ (**2a**–**e**) can be obtained in good yield (Tables I and II). The observation of a single ir NC stretching band around 2210 cm^{-1} for the isocyanide ligands in **2d**–**f** serves to infer trans square structure. The ir Pd–X stretching band in **2a**,**b**, comparable in frequency to that in **2d**–**f**, is consistent with the trans square structure. They are quite thermally stable and inert too. For example, on heating **2d** at 80° in benzene containing PPh$_3$, substitution of the isocyanide ligands takes place to give **2a** leaving the Pd–C(O)OR bond intact. However, the phenyl ester again undergoes decarbonylation producing diphenyl carbonate. Similarly the phenyl ester with "Pd(t-BuNC)$_2$" yields diphenyl carbonate and the known univalent compound [PdCl(t-BuNC)$_2$]$_2$[23] (66%). A common pattern for reactions of the phenyl ester emerges, namely decarbonylation accompanied by one-electron reduction of metal moiety (Scheme III). The formation of diphenyl carbonate is accounted for by reaction of unreacted phenyl chloroformate with the metal phenoxide. It seems plausible that the unstable C$_6$H$_5$O–M bond derived from the phenoxycarbonyl metal undergoes homolytic fission.

Oxidative addition of acyl and aroyl halides to palladium phosphine and isocyanide complexes yields the expected stable σ-acyl and aroyl compounds (Table V).

The oxidative addition of alkyl halides can involve a variety of mechanisms,[24–28] which appear to vary de-

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(23) S. Otsuka, Y. Tatsuno, and K. Ataka, *J. Amer. Chem. Soc.*, **93**, 6705 (1971).

(24) For review, see J. P. Collman and W. R. Roper, *Advan. Organometal. Chem.*, 7, 53 (1968); R. Ugo, *Coord. Chem. Rev.*, 3, 319 (1968);

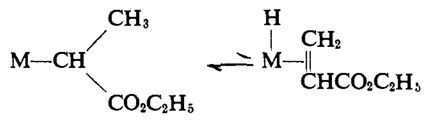
Table V. Properties of Acyl–Palladium Complexes

No.	Compound[a]	Mp, °C	Ir, cm^{-1} [b] $\nu_{C\equiv N}$	$\nu_{C=O}$	ν_{Pd-X}	Nmr, τ[c] *t*-Bu	CH$_3$
3a	$PdCl(COCH_3)(PPh_3)_2$	166–172 dec		1680	327		8.6 (s)
3b	$PdCl(COC_6H_5)[P(OPh)_3]_2$	129–132		1670	322		
3c	$PdCl(COCH_3)(t\text{-}BuNC)_2$	105–110	2195	1708	312	9.23 (s)	7.63 (s)
3d	$PdCl(COC_6H_5)(t\text{-}BuNC)_2$	135–136 dec	2197	1655	320	9.40 (s)	

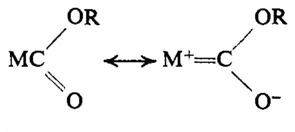
[a] All compounds listed here are colorless. Satisfactory elemental analysis were obtained for all. [b] Nujol mull. [c] In C_6D_6 for **3c**,**d** and in $CDCl_3$ for the rest with TMS as internal reference.

pending upon not only the reagents but also the reaction medium. The stereochemistry of addition of alkyl halides is, albeit important in elucidating mechanism, an unsettled issue even for the extensively investigated Ir(I) systems and has not been studied for nickel triad.

When optically active ethyl α-bromopropionate is added to a solution of "Pd(*t*-BuNC)$_2$" in ether at −30°, the reaction mixture becomes a deep red suspension after some 10 min. The color change and precipitation indicate complexation, but since the adduct is colorless (*vide infra*) and soluble in ether, the oxidative addition has not occurred at this stage. The precipitates slowly disappear near 0° giving a yellow solution from which is isolated the colorless adduct $PdBr(CH_3CHCO_2C_2H_5)(t\text{-}BuNC)_2$. The addition takes place in *n*-hexane with similar color change giving the adduct in better quality and in better yield (precipitation prevents the decomposition). The single NC stretching absorption at 2240 cm^{-1} suggests a trans alignment of the two *t*-BuNC ligands and the carbonyl band at 1700 cm^{-1} appears to be reasonable for the carbethoxy group attached to the σ-bonded carbon when compared to that (1685 cm^{-1}) of the analogous complex $PdBr(CH_2CO_2C_2H_5)(t\text{-}BuNC)_2$. Thus the adduct is assigned α-(carbethoxy)ethyl complex. This is the first isolated Pd(II) complex involving a σ-bonded *sec*-alkyl group without having a stabilizing chelation. It is thermally stable in the solid state; although quite unstable in solution, the life time is long enough to allow optical measurements. The optical activity measured immediately after dissolution in benzene was found to be nil. β-Hydrogen elimination common to alkyl compounds of Ni(II)[1,29] and other transition metals (*e.g.*, Rh(III)[30]) is unavoidable; ethyl acrylate and propionate are detected in this case and styrene and ethylbenzene in the addition of α-phenethyl chloride to $Ni(PPh_3)_3$. An equilibrium involving the σ–π rearrangement could be responsible for the racemization. The oxidative addition should then be examined with an alkyl halide having no β-hydrogen atom. The addition of optically active ethyl bromophenylacetate to "Pd(*t*-BuNC)$_2$" carried out similarly in *n*-hexane yields a yellow, optically inactive adduct $PdBr[CH(C_6H_5)CO_2C_2H_5](t\text{-}BuNC)_2$. The results strongly argue against a mechanism involving a multicentered transition state of low polarity.



Carbon–Metal Bonding in M–C(O)OR and M–COR. The remarkably facile decarbonylation and decarboxylation observed for the acyl and alkoxycarbonylnickel compounds deserve scrutiny. The stability of the Ni–C(O)OR bond in $NiX(COOR)L_2$ is apparently enhanced with PPh_3 as the biphillic ligand L rather than with *t*-BuNC. The electron-donating property falls in the order of PPh_3 > *t*-BuNC as inferred from the ir carbonyl stretching data, *e.g.*, 1670 cm^{-1} for **2e** and 1656 and 1672 cm^{-1} for **2a** (Table II). Then the ready decarboxylation observed for nickel isocyanide systems appears to suggest destabilization of the σ-carbon–metal bond by the presence of electron-accepting ligands. An enhanced back-donation from metal to the alkoxycarbonyl group reflects the lower carbonyl stretching frequency (Table II) as is the case for acyl–metal bondings.[31] One might assume an important contribution to the stability of this dπ–pπ type bonding as suggested by King and coworkers.[32] For the isostructural complexes of type $MX(CO_2R)L_2$ the carbonyl frequencies are much higher in palladium compounds (**2a** and **2b**) than in nickel compounds (**1a** and **1b**) (see Table II). The relative stability is just the reverse order to what we expect from this spectroscopic property. This contradiction can be rationalized by introduction of another resonance structure, an ionic interaction $M^+C^-(O)OR$. In the case of the palladium complexes an increase in contribution of the ionic interaction seems more than likely to offset any decrease in contribution of back-bonding. Such an ionic interaction must be a minor factor stabilizing the Ni–C(O)OR bonds. The ready alkyl migration accompanied by decarboxylation observed for the isocyanide nickel complexes has been ascribed to the formation of a cyclic intermediate assisted by the favorable geometry.



A. J. Deeming, "MTP International Review of Science," Vol. 9, Butterworths, London, 1972, pp 117–158.

(25) R. G. Pearson and W. R. Muir, *J. Amer. Chem. Soc.*, 92, 5519 (1970).

(26) J. A. Labinger, R. J. Braus, D. Dolphin, and J. A. Osborn, *J. Chem. Soc. D*, 612 (1970). The claim of inversion for *trans*-1-bromo-2-fluorocyclohexane addition to a square Ir(I) complex has been withdrawn.[27]

(27) J. S. Bradley D. E. Connor, D. Dolphin, J. A. Labinger, and J. A. Osborn, *J. Amer. Chem. Soc.*, 94, 4043 (1972).

(28) R. Ugo, A. Pasini, A. Fusi, and S. Cenini, *J. Amer. Chem. Soc.*, **94**, 7364 (1972).

(29) C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 6777 (1970).

(30) R. Cramer, *Accounts Chem. Res.*, **1**, 186 (1968).

(31) M. C. Baird, J. T. Mague, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc. A*, 1347 (1967).

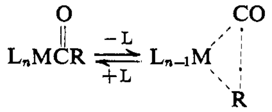
(32) R. B. King, M. B. Bisnette, and A. Fronzaglia, *J. Organometal. Chem.*, 4, 256 (1965).

Table VI. Thermal Reactions of Alkyl or Aryl–Nickel and Palladium Complexes

	Solvent	Temp, °C	Reaction time, hr	Products[a] (yield, %)[b]
$NiBr(n\text{-}C_6H_{13})(PPh_3)_2$	Toluene	20	1	2-Hexene (cis, trans) (44) *n*-Hexane (36)
$NiCl[CH(Ph)CH_3](PPh_3)_2$	Ether	20	48	Styrene (43) Ethylbenzene (12)
$PdCl[CH(Ph)CH_3](PPh_3)_2$	Benzene	130	1	Styrene (65) Ethylbenzene (18)
$NiBr(CH_2Ph)(PPh_3)_2$	Ether–benzene	20	0.2	1,2-Diphenylethane (~100)
$NiBr(CH_2CO_2C_2H_5)(PPh_3)_2$	Ether	20	48	Diethyl succinate (8) Diethyl fumarate (2)
$NiBr(CHPh_2)(PPh_3)_2$	Ether	0	24	Tetraphenylethane (34)
$NiBr(Ph)(PPh_3)_2$	Toluene	80	0.2	Biphenyl (~100)
$NiBr(\alpha\text{-Naph})(PPh_3)_2$	Toluene	110	0.2	α,α'-Binaphthyl (85)

[a] Univalent nickel or palladium complexes, $MX(PPh_3)_3$, were obtained in good yield. [b] Based on alkyl (or aryl) complex.

A similar line of reasoning may be made for the relative stability of σ-acyl and aroyl bonds in nickel and palladium compounds. So far no stable σ-acyl and aroylnickel compounds have been reported whereas the palladium compounds are stable enough to be isolated. The back-bonding as reflected in the carbonyl stretching frequency (compare ν_{CO} for **3a** *vs.* **3c** and **3b** *vs.* **3d**) decreases in the order of $PPh_3 > t\text{-BuNC} > P(OPh)_3$. The remarkable thermal stability of **3b** suggests again that the $d\pi$–$p\pi$ bonding does not play an important part for the palladium complexes. It appears rather difficult to reconcile the marked tendency of Ni–C(O)R to eliminate CO against the enhanced $d\pi$–$p\pi$ bonding exhibited in the carbonyl stretch. A mechanism involving a three-center transition state is generally accepted for the carbonyl insertion reaction. The transition state should also be involved in the reverse reaction and demands expansion of coordination. The marked propensity of Ni(II) ions compared to Pd(II) ions to form a higher coordination number could be a driving force for $NiX(COR)L_2$ to assume the proper transition-state configuration. A closely related phenomenon may be β-hydrogen elimination of $Pt(n\text{-}C_4H_9)_2(PPh_3)_2$ which occurs only after a phosphine ligand is dissociated.[33] Alternatively, a decomposition scheme involving direct homolytic cleavage of the M–C(O)R bond may account for the observed reduction of the Ni(II) ion. However, the decarbonylation of $NiCl(COC_6H_5)(PPh_3)_2$ leading to the aryl compound $NiCl(C_6H_5)(PPh_3)_2$ is best explained by assuming the cyclic transition state. The isolation of a σ-benzoyl–nickel complex $NiCl(COC_6H_5)L_2$ (L = tris(bornyl)phosphite), where the bulky phosphite ligand apparently prevents expansion of coordination around Ni(II), provides further support for our interpretation on the marked tendency of acyl–nickel(II) complexes for decarbonylation.



$$L_nM\overset{\overset{O}{\|}}{C}R \underset{+L}{\overset{-L}{\rightleftharpoons}} L_{n-1}M\begin{smallmatrix}CO\\ \vdots\\ R\end{smallmatrix}$$

Owing to the isocyanide stretching bands a comparison can be made on the $d\pi$-accepting property of an alkoxycarbonyl ligand and of the corresponding acyl ligand. The frequencies 2205 cm^{-1} for **2d** and 2195 cm^{-1} for **3c** indicate the methoxycarbonyl group to be a stronger $d\pi$-acceptor relative to the acetyl group.

Thermal Reaction of Alkyl and Arylmetal Compounds. It is generally assumed that thermal decomposition of organonickel compounds involves homolytic carbon–nickel bond fission. Indeed, methyl radical is formed in the thermal decomposition of $Ni(h^3\text{-}C_3H_5)(CH_3)$[34] and $Ni(h^5\text{-}C_5H_5)(CH_3)(PPh_3)$.[35] Although ethyl radicals are postulated for butane formation from $Ni(C_2H_5)_2(bipy)$,[36] an alternate reaction pathway can accomodate the thermal decomposition. The fate of organic moiety in thermal decomposition of organonickel compounds of type $MX(R)L_2$ has not received much attention. Among several possible modes of fragmentation,[37] (a) radical fission and (b) alkene elimination are considered to be the principal ones. The organic group in $NiX(R)L_2$ examined here are aryl or alkyl groups with or without β-hydrogen atom. The results (see Table VI) are summarized as follows.

(1) A primary and secondary alkyl group containing β hydrogen decomposes into an olefin and an alkane. The absence of a coupling product and the formation of an olefin and the corresponding alkane are consistent with reaction pathway b. That *n*-hexylnickel produces only 2-hexene deserves comment. A brief study was made on the isomerization of 1-hexene with $NiBr(PPh_3)_3$, which is a species closely related to the hydrido complex $NiX(H)(PPh_3)_2$ and actually formed in the thermal decomposition $NiX(R)(PPh_3)_2$ carried out in the presence of 1 mol of PPh_3. The result indicates that under a comparable condition (20°, 1 hr) the isomerization is incomplete yielding 2-hexene in 63% yield together with a small amount of other hexenes. The absence of 1-hexene in the thermal decomposition of $NiBr(hexyl)(PPh_3)_2$ is not surprising since the hydrido species and 1-hexene, if they were the initial products, should exist in equimolar amounts. The absence of other hexenes in the thermal decomposition implies kinetic control. Such a deviation from the thermodynamic equilibrium was beautifully demon-

$$\text{(a)}\ RCH_2CH_2M^{II} \longrightarrow M^I + RCH_2CH_2\cdot$$

$$RCH_2CH_2\cdot \longrightarrow {}^1\!/_2RCH{=}CH_2 + {}^1\!/_2RCH_2CH_3$$

$$\text{(b)}\ RCH_2CH_2M^{II} \longrightarrow M^{II}H + RCH{=}CH_2$$

$${}^1\!/_2RCH{=}CH_2 + M^{II}H \longrightarrow M^I + {}^1\!/_2RCH_2CH_3$$

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(33) G. M. Whitesides, J. F. Gasch, and E. R. Stedronsky, *J. Amer. Chem. Soc.*, **94**, 5258 (1972).

(34) B. Bogdanovič, H. Bönneman, and G. Wilke, *Angew. Chem., Int. Ed. Engl.*, **5**, 582 (1966).

(35) J. Thomson and M. C. Baird, *Can. J. Chem.*, **48**, 3443 (1970).

(36) T. Saito, Y. Uchida, A. Misono, A. Yamamoto, K. Morifuji, and S. Ikeda, *J. Amer. Chem. Soc.*, **88**, 5198 (1966).

(37) R. P. A. Sneeden and H. H. Zeiss, *J. Organometal. Chem.*, **22**, 713 (1970).

Table VII. Olefin Insertion Reactions into Alkyl or Aryl–Nickel and Palladium Complexes

	Olefin[a]	Solvent	Temp, °C	Reaction time, hr	Organic products (% yield)[b]
$NiBr(Ph)(PPh_3)_2$	ST	ST	80	0.2	*trans*-Stilbene (85), 1,2-diphenylethane (4)
$NiBr(Ph)(PPh_3)_2$	MA	MA	20	3	Methyl cinnamate (85)
$NiBr(Ph)(PPh_3)_2$[c]	AN	Benzene	20	24	Cinnamonitrile (15), β-phenylpropionitrile (19)
$PdBr(Ph)(PPh_3)_2$	ST	ST	110	0.5	*trans*-Stilbene (28), 1,2-diphenylethane (4)
$PdBr(Ph)(PPh_3)_2$	MA	MA	80	1	Methyl cinnamate (20)
$PdCl(CO_2CH_3)(PPh_3)_2$	ST	ST	145	1.5	Methyl cinnamate (11)
$PdCl(CO_2CH_3)(PPh_3)_2$	MA	Toluene	180	2.5	Dimethyl fumarate (4)
$NiBr(CH_2CO_2C_2H_5)(PPh_3)_2$	ST	Benzene	20	1	Ethyl 4-phenyl-3-butenoate (21)

[a] ST = styrene, MA = methyl acrylate, AN = acrylonitrile. [b] Based on alkyl (or aryl) complex. [c] Reaction was carried out in the absence of PPh_3.

strated for hydridonickel-catalyzed isomerization of 4-methyl-1-pentene to 4-methyl-2-pentene.[38] These results contrast the absence of 2-butene in the thermal decomposition of $Pt(n\text{-}C_4H_9)_2(PPh_3)_2$;[33] the observed exclusive formation of 1-butene is rather unusual in view of the rapid scrambling of deuterium in the α and β positions. We consider that the complete isomerization to 2-hexene substantiates the hydride formation and hence the β elimination.

(2) An alkylnickel compound without β-hydrogen undergoes homolytic fission producing the alkyl coupling product (Table VI) and a reduced nickel compound. Thus the benzylnickel from benzyl bromide and $Ni(PPh_3)_4$ gives quantitatively 1,2-diphenylethane and $NiBr(PPh_3)_3$. The same reaction pattern is also observed for the alkylnickel compounds derived from $BrCH(C_6H_5)_2$. Interestingly thermal decomposition of $NiBr(CH_2CO_2C_2H_5)(PPh_3)_2$ formed *in situ* gives a small amount (2%) of diethyl fumarate in addition to diethyl succinate. The dehydrohalogenation similar to carbenoid reactions has not been demonstrated in organotransition metal decomposition reactions. So far this unusual α elimination has been observed only for the reaction of α-bromoacetic acid with a nickel(0) compound.

(3) Arylnickel compounds $NiX(Ar)(PPh_3)_2$, which are thermally fairly stable, afford upon heating (80–100°) biaryl in quantitative yield. For a direct reaction between bis(cyclooctadiene)nickel and 2 mol of aryl halide to produce biaryl, Semmelhack, *et al.*,[39] postulated oxidative addition of the aryl halide to an intermediate $NiX(Ar)L_2$ and subsequent coupling of the two σ-aryl ligands in $NiX_2(Ar)_2$. As we employed an isolated $NiX(Ar)(PPh_3)_2$, without adding free aryl halide, the thermal decomposition may follow a different mechanism. In the presence of 1 mol of PPh_3, the univalent nickel compound $NiX(PPh_3)_3$ was isolated.

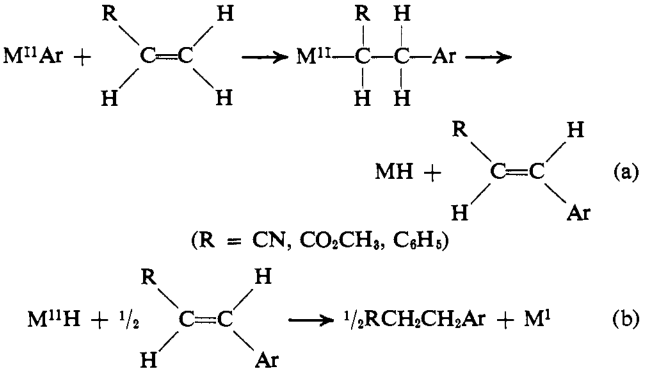
Insertion Reactions. Alkoxycarbonyl, acyl (or aroyl), and alkyl (or aryl) nickel and palladium compounds of type $MX(R)L_2$ were examined for insertion of CO, RNC, and olefins.

Carbon monoxide does not insert into the alkoxycarbonyl-metal and acyl-metal bond. Polycarbonyl or pyruvic acid derivatives are not therefore accessible by this route. Carbon monoxide insertion into a σ-alkyl or aryl–metal bond is well known. However, the thermal instability of acylnickel species suggests that the carbon monoxide insertion reaction of alkylnickel species is not promising unless some special device is used for the auxiliary ligand. In fact, the insertion is achieved and $NiCl(COC_6H_5)L_2$ is obtained from $NiCl(C_6H_5)L_2$ (L = tris(bornyl)phosphite).

An alkyl isocyanide, *e.g.*, *t*-BuNC, does not add to the alkoxycarbonyl compounds of both Ni(II) and Pd(II) ions. As shown in the preceding section, the insertion to σ-acyl or aroylnickel compounds does occur to give interesting polyimino compounds,[3] *i.e.*, polycarbonyl derivatives.

Reaction of an olefin with alkoxycarbonylnickel compounds fails to give tractable organic compounds, whereas the reaction with the palladium compound produces a carboxylate-substituted olefin. For example, $PdCl(COOCH_3)(PPh_3)_2$ reacts at high temperature (100–180°) with styrene and methyl acrylate affording respectively methyl cinnamate and dimethyl fumarate (Table VII). Reduction of palladium(II) compounds is observed for both cases. Accordingly this olefin substitution reaction is best explained by a reaction scheme analogous to the substitution reaction with alkylpalladium compounds (*cf.* Scheme IV), *i.e.*, insertion of an olefin into the Pd–C(O)OR bond followed by β-hydrogen elimination. Heck[40] employed for olefin carboxylation a combination of $Pd(OAc)_2$ and $Hg(CO_2CH_3)(OAc)$ which is assumed to produce carbomethoxypalladium acetate species.

Scheme IV



Finally, we note briefly the reactions of organometal derivatives with olefins. The results summarized in

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(38) G. Lefevre and Y. Chauvin, *Aspects Homogeneous Catalysis*, **1**, 108 (1970).

(39) M. F. Semmelhack, P. M. Helquist, and L. D. Jones, *J. Amer. Chem. Soc.*, **93**, 5908 (1971).

(40) R. F. Heck, *J. Amer. Chem. Soc.*, **91**, 6707 (1969); **93**, 6896 (1971).

Table VII are in accord with reaction Scheme IV, *i.e.*, coordination of an olefin, intramolecular alkyl migration, and β-hydrogen elimination. This scheme is a corollary of our studies on the thermal reactions (the preceding section). This scheme receives support from the isolation of the corresponding alkane (Scheme IVb) and the univalent metal complex derived from either organometal or hydridometal compounds. The olefin arylation (a) is generally accompanied by side reactions producing olefin dimers and polymers. An alternative mechanism involving oxidative addition of an olefin to form a σ-vinyl (σ-aryl) metal(IV) compound and subsequent radical coupling is unlikely in view of the high promotional energy of the divalent metals. A recent study[41] using labeled styrene for the palladium-assisted olefin arylation reaction also presented results disfavoring the σ-vinyl–σ-phenyl coupling mechanism.[42] A stable σ-alkylpalladium species, *e.g.*, $PdBr(CH_2CO_2C_2H_5)(PPh_3)_2$, is generally reluctant to olefin insertions.

The detailed mechanism and stereochemistry of these olefin substitution reactions assisted by nickel(II) or palladium(II) compounds will be subjects of future publications.

Experimental Section

Ir spectra were measured using Nujol mulls with a Hitachi-Perkin Elmer 225 spectrometer, nmr spectra with a Jeol JNM-4H-100 or JNM-C-60HL, mass spectra with a Hitachi RMU-7HR, molecular weight by vapor pressure osmometry in benzene solution with a Hitachi Perkin-Elmer 115 or by cryoscopy in benzene solution, and glpc with a Yanagimoto GCG-550TFP or Shimadzu GC-2C with a column packed with Apiezon-Grease-L, PEG-6000, $AgNO_3$–$PhCH_2CN$, active charcoal, or silica gel. All reactions involving organometallics were carried out under pure nitrogen. Only typical examples of each reaction type are given below.

Oxidative Addition. (a) Methyl Chloroformate to $Ni(PPh_3)_4$. A solution of methyl chloroformate (0.06 ml in 1 ml of toluene, slight excess) was added to a stirring suspension of $Ni(PPh_3)_4$ (0.85 g, 0.77 mmol) in 35 ml of toluene. The mixture was stirred for 5 hr at room temperature to produce a yellow fine precipitate which was filtered, washed with *n*-hexane, and dried *in vacuo*. The yellow solid was the thermally unstable, very air-sensitive alkoxycarbonyl complex, $NiCl(CO_2CH_3)(PPh_3)_2$ (0.36 g, 0.53 mmol, 69%).

(b) Benzyl Chloroformate to Ni(*t*-BuNC)$_4$. A solution of $ClCO_2CH_2C_6H_5$ in toluene (0.85 ml, containing 1.4 mmol) was slowly added to a stirring solution of Ni(*t*-BuNC)$_4$ (0.54 g, 1.4 mmol) in 10 ml of toluene. After stirring for 15 hr at room temperature, the solvent was removed *in vacuo*. The reddish orange solid residue was recrystallized from toluene–*n*-hexane to give an orange microcrystalline complex, NiCl[(C=NBu-*t*)$_3$CH$_2$C$_6$H$_5$](*t*-BuNC) (0.42 g, 0.82 mmol, 60%).

(c) Ethyl Chloroformate to Ni(*t*-BuNC)$_4$. A mixture of $ClCO_2C_2H_5$(0.32 ml, slight excess) and Ni(*t*-BuNC)$_4$ (0.92 g, 2.4 mmol) in 20 ml of benzene was refluxed under nitrogen giving a dark brown solution. The solvent was removed *in vacuo*. The dark brown oily residue was recrystallized from toluene–*n*-hexane to give a brown complex, [NiCl(*t*-BuNC)$_2$]$_n$ (0.35 g, 56%).

(d) Phenyl Chloroformate to Ni(*t*-BuNC)$_4$. To a stirring suspension of Ni(*t*-BuNC)$_4$ (0.35 g, 0.9 mmol) in 15 ml of *n*-hexane was added $ClCO_2Ph$ (0.12 ml, 0.9 mmol) at room temperature. After 2 days, dark brown precipitates and a pale yellow brown solution were obtained. From the mother liquor, pale yellow needles of Ni(CO)(*t*-BuNC)$_3$ (14% yield on metal) and colorless needles of PhOCOOPh (28% yield on $ClCO_2Ph$) were obtained. The majority of the nickel-containing products (dark brown precipitates) was not identified because of instability.

(e) Alkyl Chloroformates to Pd(0) Complexes. Methyl chloroformate (0.1 ml, slight excess) was added to a stirring suspension of "Pd(*t*-BuNC)$_2$" (0.34 g, 1.3 mmol) in 10 ml of toluene at −78°. During stirring for 30 min, the temperaure was allowed to reach ambient temperature. After another hour at room temperature, the pale brown solution was evaporated *in vacuo*. The solid residue was recrystallized from toluene–*n*-hexane producing the stable alkoxycarbonyl complex, PdCl(CO$_2$CH$_3$)(*t*-BuNC)$_2$, as colorless prisms (0.30 g, 0.81 mmol, 65%).

Similarly the following alkoxycarbonyl complexes were prepared from the corresponding alkyl chloroformate and $Pd(PPh_3)_4$ or $Pd[P(OPh)_3]_4$. The solvent, reaction time, temperature, and yield are shown in the parentheses: $PdCl(CO_2CH_3)(PPh_3)_2$ (benzene, 5 hr, 80°, 83%), $PdCl(CO_2C_2H_5)[P(OPh)_3]_2$ (toluene, 1 hr, 110°, 95%).

(f) Phenyl Chloroformate to $Pd(PPh_3)_4$. A mixture of phenyl chloroformate (0.03 ml, 0.23 mmol) and $Pd(PPh_3)_4$ (0.26 g, 0.23 mmol) in 10 ml of toluene was stirred at 80° for 30 min producing pale reddish orange solution. Addition of *n*-hexane (10 ml) gave a small amount of pale yellow microfine crystals of formula $PdCl(PPh_3)_3$. The instability in solution prevented molecular weight measurement.

Anal. Calcd for $C_{54}H_{45}ClP_3Pd$: C, 69.84; H, 4.88; Cl, 3.82. Found: C, 70.42; H, 4.76; Cl, 4.41.

(g) Phenyl Chloroformate to "Pd(*t*-BuNC)$_2$." Similar reaction between phenyl chloroformate (0.15 ml, 1.1 mmol) and "Pd(*t*-BuNC)$_2$" (0.22 g, 0.8 mmol) in 15 ml of toluene at room temperature produced a pale yellow slurry containing a yellow powdery precipitate. The yellow precipitate was separated by filtration, washed with *n*-hexane, and dried *in vacuo*; the filtrate was concentrated to give the same yellow compound, [PdCl(*t*-BuNC)$_2$]$_2$ (total yield 0.19 g, 0.27 mmol, 66%). From the mother liquor was obtained a colorless crystalline compound which could readily be identified as diphenyl carbonate.

(h) Acetyl Halides to $Ni(C_2H_4)(PPh_3)_2$. To a stirring solution of $Ni(C_2H_4)(PPh_3)_2$ (0.51 g, 0.84 mmol) in 15 ml of toluene was added CH_3COCl (0.07 ml, slight excess) at room temperature. Stirring for 30 min at room temperature followed by addition of 5 ml of *n*-hexane gave $NiCl(PPh_3)_3$ as yellow microcrystals (0.15 g, 0.18 mmol, 21%). From the filtrate were isolated nickel(0) carbonyl complexes $Ni(CO)_2(PPh_3)_2$ and $Ni(CO)_3(PPh_3)$. A similar reaction of CH_3COI with $Ni(C_2H_4)(PPh_3)_2$ gave only $NiI_2(PPh_3)_2$ as dark brown solids (74%).

(i) Benzoyl Chloride to $Ni(PPh_3)_4$. To a stirring solution of $Ni(PPh_3)_4$ (0.38 g, 0.32 mmol) in 10 ml of toluene was added ClCOPh (0.038 ml) at 0°. Immediately the color changed to reddish orange. After stirring for 20 hr at room temperature, the solvent was removed *in vacuo*. Upon addition of a small amount of *n*-hexane, $NiCl(Ph)(PPh_3)_2$ was obtained as a yellow microcrystalline complex (0.20 g, 0.28 mmol, 87%). Nickel carbonyl derivatives $Ni(CO)_3(PPh_3)$ and $Ni(CO)_2(PPh_3)_2$ were obtained from the filtrate.

(j) Acetyl Chloride to Ni(*t*-BuNC)$_4$. To a stirring suspension of Ni(*t*-BuNC)$_4$ (1.2 g, 3 mmol) in 20 ml of *n*-hexane was added CH_3COCl (0.25 ml) at room temperature. Stirring being continued for 3 hr at room temperature, a brown precipitate appeared in the red-orange solution. From the mother liquor were isolated reddish orange NiCl[(C=NBu-*t*)$_4$COCH$_3$](*t*-BuNC) (0.11 g, 0.2 mmol, 7%), orange NiCl[(C=NBu-*t*)$_3$CH$_3$](*t*-BuNC) (0.13 g, 0.3 mmol, 10%), and a small amount of carbonyl complex, Ni(CO)(*t*-BuNC)$_3$ by virtue of the difference in solubility.

(k) Acyl or Aroyl Halides to Pd(0) Complexes. A mixture of CH_3COCl (0.5 ml, excess) and "Pd(*t*-BuNC)$_2$" (0.22 g, 0.80 mmol) in 15 ml of toluene was stirred for 30 min at 0°. The pale yellow solution was concentrated *in vacuo*. Addition of a small amount of *n*-hexane afforded the thermally stable acyl complex, PdCl(COCH$_3$)(*t*-BuNC)$_2$ as pale yellow needles (0.26 g, 0.74 mmol, 92%).

Similarly a reaction of C_6H_5COCl and $Pd[P(OPh)_3]_4$ in toluene at 80° gave $PdCl(COPh)[P(OPh)_3]_2$ (64%).

(l) (*S*)-(−)-Ethyl α-Bromopropionate to "Pd(*t*-BuNC)$_2$." (*S*)-(−)-Ethyl α-bromopropionate (0.3 ml, 2.5 mmol, $[\alpha]^{28}\mathrm{D}$ −7.4°, *c* 1.7, C_6H_6) was added to a suspension of "Pd(*t*-BuNC)$_2$" (0.34 g, 1.25 mmol) in 10 ml of *n*-hexane at −40 to −30°. The temperature being allowed to reach slowly to 0° during 3 hr of stirring (the original orange-red color of the suspension changes to deep red at −20 to −10°), a yellow precipitate appeared in the solution. The precipitates were separated by decantation, washed with *n*-hexane, and recrystallized from cold ether twice to give colorless crystals of formula PdBr(CH$_3$CHCO$_2$C$_2$H$_5$)(*t*-BuNC)$_2$ (0.20 g, 0.44

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[41] R. S. Shue, *J. Amer. Chem. Soc.*, **93**, 7116 (1971).

[42] I. Moritani, S. Danno, Y. Fujiwara, and S. Teranishi, *Bull. Chem. Soc. Jap.*, **44**, 578 (1971), and prior papers of this series, in particular the following paper: S. Danno, I. Moritani, and Y. Fujiwara, *Tetrahedron*, **25**, 4819 (1969).

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mmol, 35%), mp 75° dec. In ether the same compound was obtained in a poor yield with ethyl acrylate and ethyl propionate. This compound can be dissolved in cold benzene without appreciable deterioration for some minutes, but the solution slowly decomposed at room temperature as indicated by conspicuous color change to yellow; the yellow compound was isolated from the solution and identified as $[\mathrm{PdBr}(t\text{-BuNC})_2]_2$.[23] The optical rotation measured at 22° immediately after dissolution in benzene was found to be nil. Ir (Nujol): 2240 cm^{-1} (ν_{CN}), 1700 (ν_{CO}).

Anal. Calcd for $C_{15}H_{27}N_2O_2BrPd$: C, 39.71; H, 6.00; N, 6.17. Found: C, 40.19; H, 6.04; N, 6.16.

(m) (*S*)-(+)-Ethyl Bromophenylacetate to "Pd(*t*-BuNC)$_2$." (*S*)-(+)-Ethyl bromophenylacetate (0.34 g, 1.4 mmol, $[\alpha]^{24}\mathrm{D}$ +56.4°, *c* 1.65, ethanol) was added to a suspension of "Pd(*t*-BuNC)$_2$" (0.38 g, 1.4 mmol) at −78°. Under stirring the temperature was allowed to reach to room temperature during a few hours. Similar treatment as above produced $\mathrm{PdBr(PhCHCO_2C_2H_5)}(t\text{-BuNC})_2$ (0.22 g, 0.4 mmol, 30%) as yellow crystals showing no optical activity in CH_2Cl_2 at 24°, mp 95–97.5° dec. Ir (Nujol): 2200 cm^{-1} (ν_{CN}), 1695 (ν_{CO}).

Anal. Calcd for $C_{20}H_{29}N_2O_2BrPd$: C, 46.58; H, 5.67; N, 5.43; Br, 15.49. Found: C, 46.45; H, 5.77; N, 5.34; Br, 15.33.

(*n*) Methyl Bromoacetate to "Pd(*t*-BuNC)$_2$." To a stirring suspension of "Pd(*t*-BuNC)$_2$" (0.20 g, 0.75 mmol) in 20 ml of *n*-hexane was added $BrCH_2CO_2CH_3$ (0.1 ml, excess) at −78°. The temperature was allowed to reach room temperature. After 3 hr of stirring at ambient temperature, the yellow crystalline precipitate was isolated and recrystallized from toluene–*n*-hexane to give $[\mathrm{PdBr}(t\text{-BuNC})_2]_2$[23] (0.025 g, 10%) and *trans*-$\mathrm{PdBr(CH_2CO_2CH_3)}(t\text{-BuNC})_2$ (0.25 g, 78%) as colorless crystals, mp 101–104° dec (in air). The latter was identified from elemental analysis and the spectral data. Nmr (C_6D_6): τ 6.53 (s, 3H, CH_3), 7.45 (s, 2H, CH_2), and 9.15 (s, 18, *t*-Bu). Ir (Nujol): 2205 cm^{-1} (ν_{CN}) and 1695 (ν_{CO}).

Anal. Calcd for $C_{13}H_{23}N_2O_2BrPd$: C, 40.96; H, 6.08; N, 7.35. Found: C, 40.76; H, 5.98; N, 7.10.

Thermal Reactions of Alkyl or Aryl–Nickel and Palladium Complexes. The following alkyl complexes were prepared *in situ* by mixing the alkyl halides and zerovalent nickel or palladium complexes in solution and subjecting the solution to thermal decomposition: $\mathrm{NiCl[CH(Ph)CH_3](PPh_3)_2}$, $\mathrm{NiBr}(n\text{-}C_6H_{13})\mathrm{(PPh_3)_2}$. $\mathrm{NiBr(CH_2Ph)(PPh_3)_2}$, $\mathrm{NiBr(CH_2CO_2H_5)(PPh_3)_2}$. $\mathrm{NiBr(CH_2CO_2C_2H_5)}(t\text{-BuNC})_2$, $\mathrm{PdCl[CH(Ph)CH_3](PPh_3)_2}$, and $\mathrm{PdBr(CH_2CO_2C_2H_5)}(t\text{-BuNC})_2$.

The following aryl–nickel complexes were isolated in a pure state and subjected to thermal reactions: $\mathrm{NiBr(Ph)(PPh_3)_2}$ and $\mathrm{NiBr}(\alpha\text{-Naph})\mathrm{(PPh_3)_2}$.[43] Solvent, temperature, reaction time, and organic products are listed in Table VII.

Olefin Insertion Reactions. The following alkyl or aryl–nickel and palladium complexes were treated with olefins in the presence of PPh_3: $\mathrm{NiBr(Ph)(PPh_3)_2}$, $\mathrm{PdBr(Ph)(PPh_3)_2}$, and $\mathrm{PdCl(CO_2CH_3)(PPh_3)_2}$. For the reaction of unstable alkyl complexes, *e.g.*, $\mathrm{NiBr(CH_2CO_2C_2H_5)(PPh_3)_2}$, the organometal compounds were prepared in the presence of olefins. Main organic products and their yield were determined by glpc method (Table VII). Some typical examples are shown below.

(a) Reaction of Styrene with $\mathrm{MBr(Ph)(PPh_3)_2}$ (M = Pd, Ni). A mixture of $\mathrm{PdBr(Ph)(PPh_3)_2}$ (0.20 g, 1.17 mmol) and PPh_3 (0.04 g, 0.17 mmol) in 3 ml of styrene was heated at 110° for 0.5 hr. After usual work-up with ether, the ether extract was analyzed by glpc on Apiezou-Grease-L (0.7 m, 180°, 1.3 atm) showing the presence of *trans*-stilbene (28%) and 1,2-diphenylethane (4%) at 11.3 and 3.8 min, respectively. A similar reaction of $\mathrm{NiBr(Ph)(PPh_3)_2}$ under the same condition as above produced styrene oligomers, *trans*-stilbene and 1,2-diphenylethane in ratio of 192:21:1, respectively.

(b) Reaction of Styrene with $\mathrm{PdCl(CO_2CH_3)(PPh_3)_2}$. A mixture of $\mathrm{PdCl(CO_2CH_3)(PPh_3)_2}$ (0.23 g, 0.2 mmol) and PPh_3 (0.11 g, 0.4 mmol) in 3 ml of styrene was heated at 145° for 1.5 hr. The glpc analysis on PEG-6000 (0.7 m 180°, 1.5 atm) showed the formation of methyl cinnamate and four unidentified products in ratio of 12:2.5:5:1:5 at 5.2, 10.6. 14.0. 19.0, and 21.0 min. respectively.

(c) Reaction of $BrCH_2CO_2C_2H_5$ with $\mathrm{Ni(PPh_3)_3}$ in the Presence of Styrene. To a suspension of $\mathrm{Ni(PPh_3)_3}$ (1.83 g, 2.1 mmol) in 4 ml of benzene–styrene (1:1) was added $BrCH_2CO_2C_2H_5$ (0.24 ml, 2.1 mmol) and the mixture was stirred for 1 hr at room temperature. After filtration of yellow precipitate, $\mathrm{NiBr(PPh_3)_3}$ (1.3 g, 68%), the organic product was analyzed by glpc (Apiezon-Grease-L) with only one major peak being detected. This was assigned as ethyl 4-phenyl-3-butenoate (21%) by comparing the retention time and ir and nmr spectra with those of an authentic sample.

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[43] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1718 (1960).

A Simple Correlation of Hyperfine Splitting Constants of Radical Ions and Orientation in Aromatic Substitution Reactions

Nicolaos D. Epiotis

Contribution from the Department of Chemistry, University of Washington, Seattle, Washington 98105. *Received December 2, 1972*

Abstract: The hyperfine splitting constants of radical ions can be used in order to make predictions about the preferred orientation of aromatic substitution reactions. A simple model on the basis of which such a correlation becomes possible is presented and actual experimental cases are discussed. The advantage of this approach lies in the fact that it allows predictions to be made in the case of reactions of mono- and polysubstituted aromatics where chemical intuition is insufficient for making correct predictions.

Electron spin resonance has been primarily used in connection with the study of the properties of radical ions.[1,2] The determination of spin densities has been a major research target[3] and the concomitant testing of molecular orbital theory has been of great importance.[4] On the other hand, interest in the direction of relating esr data to reactivity parameters in organic chemistry has only recently surfaced. For example, Bowers has discussed the Hammett equation in terms of esr data.[5] Perturbation theory[6] provides

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[1] E. T. Kaiser and L. Kevan, Ed., "Radical Ions," Interscience, New York, N. Y., 1968.

[2] K. W. Bowers, *Advan. Magn. Resonance*, **1**, 317 (1965).

[3] B. H. J. Bielski and J. M. Gebicki, "Atlas of Electron Spin Resonance Spectra," Academic Press, New York, N. Y., 1967; see also ref 2.

[4] J. R. Bolton and G. K. Fraenkel, *J. Chem. Phys.*, **40**, 3307 (1964); G. Vincow, in ref 1.

[5] K. W. Bowers, in ref 1.