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BONDING AND REACTIVITY IN π-ALLYL—METAL COMPOUNDS

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Summary

The π-allyl group of π-$C_3H_5Co(CO)_3$ has two angles of tilt, one of which (from semi-empirical molecular orbital calculations) is stabilised principally by the influence of the $C(p_x)$ orbitals of the terminal carbon atoms, which form part of the σ-framework of the π-allyl group, and the other of which is stabilised by a balance between bonding orbital components of the central and terminal carbon atoms. The $Co(CO)_3$ moiety has asymmetric bonding, with one CO group more weakly bonded to the metal atom. The asymmetric bonding of the $Co(CO)_3$ moiety is primarily caused by the electronic character of the π-allyl group, but is significantly influenced by the magnitude of the τ-tilt angle of the π-allyl group. The relatively high reactivity of π-$C_3H_5Co(CO)_3$, compared with the reactivity of π-$C_3H_5Fe(CO)_2NO$, $Co(NO)(CO)_3$, or $Ni(CO)_4$, is explained by the relatively weak bonding of a CO group to the metal atom and a possible explanation of the anomalous relative rates of the reactions of π-$C_3H_4RCo(CO)_3$ (R = H, 1-CH_3, 2-CH_3, 1-Cl, 2-Cl) with $P(C_6H_5)_3$ is indicated.

The angles of tilt of the π-allyl group and the asymmetric bonding of the π-cyclopentadienyl moiety in $[\pi$-$C_3H_4Ni(\pi$-$C_5H_5)]_2$ are caused by factors similar to those in π-$C_3H_5Co(CO)_3$.

Introduction

The metal—allyl group has become of increasing interest because of its unusual intrinsic properties [1, 2] and its importance in organic syntheses [2, 3] and catalytic reactions [3, 4].

Considerable progress has recently been made in experimental aspects of metal—allyl chemistry [1—12], but theoretical treatments of the causes of the tilting of the π-allyl group are limited to overlap integral calculations using Slater orbitals [13] and qualitative discussions of the bonding in $(\pi$-$C_3H_5PdCl)_2$ [14] and between the π-allyl group and a metal atom [15]. Slater orbitals, however, have been criticised [16].

Quantum chemical calculations on metal—allyl compounds should lead to a better understanding of the compounds. and can illuminate details of metal—allyl bonding. Semi-empirical molecular orbital (MO) calculations on $(\pi\text{-}C_3H_5)_2M$ and $(\pi\text{-}C_3H_5MCl)_2$ (M = Ni, Pd, Pt) [17] and ab initio calculations on $(\pi\text{-}C_3H_5)_2Ni$ [18, 19] have been directed principally towards correlation of calculated eigenvalues with energy levels obtained from photoelectron spectra. Semi-empirical MO calculations on $(2\text{-}CH_3\text{-}\pi\text{-}C_3H_4)_2M$ [20] (M = Ni, Co, Fe, Cr) rationalise the relative stability of the Ni compound, and the relatively high reactivity of $\pi\text{-}C_3H_5Co(CO)_3$ has been explained [21]. The electronic nature of the π-allyl group is not certain, but experimental evidence of its electron-donor capacity has been obtained from ^{13}C NMR spectra of $(\pi\text{-}C_3H_5MX)_2$ (M = Pd, Pt; X = Cl, Br, I) and other π-allyl—metal compounds [22], and from the dipole moments of $\pi\text{-}C_3H_4RFe(CO)_2NO$ [23] (R = H, 2-CH_3, 2-Cl, 2-Br). The semi-empirical calculations on $(\pi\text{-}C_3H_5)_2Pd$ [24], $(\pi\text{-}C_3H_5)_2M$ [17] and $(\pi\text{-}C_3H_5MCl)_2$ [17] show the dual capacity of the π-allyl group to donate and accept electronic charge, with the electron-donor property generally predominating.

The properties of the π-allyl and other groups in the compounds $\pi\text{-}C_3H_5\text{-}Co(CO)_3$ and $\pi\text{-}C_3H_5Ni(\pi\text{-}C_5H_5)$ have been studied by self-consistent molecular orbital calculations based on the CNDO method. Results of calculations on $\pi\text{-}C_3H_5Fe(CO)_2NO$, $Co(NO)(CO)_3$, $Ni(CO)_4$ and $\pi\text{-}C_3H_4RCo(CO)_3$ (R = H, 1-CH_3, 2-CH_3, 1-Cl, 2-Cl) are also presented.

Method of calculation and structural parameters

A modified version [25] of the CNDO method [26] has been employed. The computer input parameters have been discussed previously [27].

Coordinates of the atoms were calculated from the structural parameters of $\pi\text{-}C_3H_5Co(CO)_3$ [28], and the structure of $\pi\text{-}C_3H_5Ni(\pi\text{-}C_5H_5)$ was assumed to be similar to that of $[\pi\text{-}C_3H_4Ni(\pi\text{-}C_5H_5)]_2$ [11] but with equal M—C (2.100 Å) and C—C (1.410 Å) bond lengths in the π-cyclopentadienyl—metal moiety. Dipole moment results [23] show that the nitrosyl group is *trans* to the halogen in $\pi\text{-}C_3H_4RFe(CO)_2NO$ (R = 2-Cl, 2-Br) and it is therefore reasonable to assume that the nitrosyl group is *cis*- to the π-allyl group in $\pi\text{-}C_3H_5Fe(CO)_2NO$, which was assumed to have a structure identical to that of $\pi\text{-}C_3H_5Co(CO)_3$. Structural parameters of $Ni(CO)_4$ [29] were employed. Unknown bond lengths [Co—N(O) = 1.80 Å, N—O = 1.15 Å] were estimated from a comparison of known bond lengths of similar compounds [30, 31].

Results and discussion

$\pi\text{-}C_3H_5Co(CO)_3$ has a distorted tetrahedral structure [32] with OC—M—CO angles of ca. 100°. The π-allyl group is tilted with respect to the $Co(CO)_3$ moiety [28], and in common with other π-allyl—metal compounds, has two types of tilt angle: the τ angle, which is the angle between the plane of the π-allyl carbon atoms and the plane of the carbonyl carbon atoms, and the ρ angle, which is the angle between the plane of the π-allyl carbon atoms and the plane through the metal atom and the terminal carbon atoms of the π-allyl group (Fig. 1).

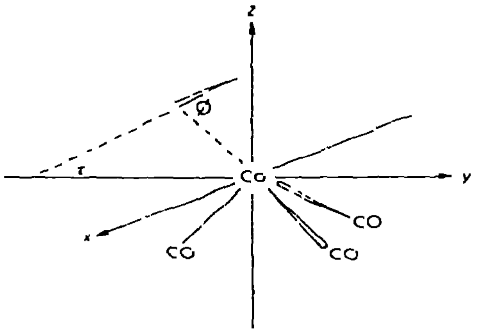

Fig. 1. Ligand distribution of π-$C_3H_5Co(CO)_3$.

The M—C (π-allyl) bond lengths (which determine the ϕ angle) are approximately equal, with the central carbon atom slightly nearer to the metal atom.

A. *Bonding in the π-allyl—metal group*

The calculations on π-$C_3H_5Co(CO)_3$ and π-$C_3H_5Ni(\pi$-$C_5H_5)$ show that the most important π-allyl—metal bonding interaction is that between the $M(d_{xz})$ orbital and the formally singly occupied molecular orbital, ψ_2 [*], which involves the p_z orbitals of the terminal carbon atoms. The central carbon atom is involved in only the bonding (ψ_1) and antibonding (ψ_3) orbitals and therefore has a considerably smaller role than the terminal carbon atoms in the π-allyl—metal bonding (Table 1).

(i) The τ angle of tilt. By varying the τ angle of π-$C_3H_5Co(CO)_3$ from 0° to 10°, 20°, 36°, 60°, while retaining all other features of the π-allyl—metal and metal—tricarbonyl moieties, the $M—C_1$ and $M—C_3$ bond indices[**] are observed to attain a maximum when $\tau = 36°$ (Table 2), which is the experimentally observed angle of tilt. As τ increases the $M(d_{xz})—C_1(p_z)$ bond index decreases, but the $M(d_{xz}, d_{xy})—C_1(p_x)$ bond indices increase and the latter increases more than offset the $M(d_{xz})—C_1(p_z)$ decreases except when $\tau = 60°$ (Table 4). The very large decrease in the $M(d_{xz})—C_1(p_z)$ bond index from $\tau = 36°$ to $\tau = 60°$ is not sufficient

TABLE 1

BOND INDICES OF π-$C_3H_5Co(CO)_3$ AND π-$C_3H_5Ni(\pi$-$C_5H_5)$

	π-$C_3H_5Co(CO)_3$			π-$C_3H_5Ni(\pi$-$C_5H_5)$				
M—C(π C_3H_5)	0.5418	0.1736	0 5418	0.4475	0.1961	0.4475		
C—C	1.4076	1.4076		1.3993	1.3993			
M—C(O)	0 5268	0.4069	0.5268					
C—O	2.4541	2.4318	2.4541					
M—C(π-C_5H_5)				0.2544	0.1752	0.2544	0.2085	0.2085
C—C				1.3276	1.3276	1.2098	1.4135	1.2098

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[*] Huckel orbitals of the π-allyl group are depicted in ref. 33.

[**] Bond index, B_{XY}, is defined by the equation $B_{XY} = \sum_{\lambda \text{ on } X} \sum_{\lambda \text{ on } Y} (\sum_{i \text{ occ.}} 2C_{i\lambda}C_{i\sigma})^2$ where $C_{i\lambda}$ is the coefficient of the atomic orbital λ of the occupied molecular orbital i.

TABLE 2

VARIATIONS OF M—C(π-allyl) BOND INDICES WITH τ AND ϕ IN π-$C_3H_5Co(CO)_3$

ϕ (°)	τ(°)	M—C_1	M—C_2	M—C_3
105	0	0.5090	0.1527	0.5090
	10	0.5241	0.1588	0.5241
	20	0.5354	0.1686	0.5354
	36	0.5418	0.1736	0.5418
	60	0.5382	0.1848	0.5382
90		0.5355	0.2125	0.5355
150		0.5311	0.1067	0.5311
Terminal carbon atoms in xz-plane				
90		0.5291	0.2055	0.5291
105		0.5295	0.1619	0.5295
150		0.5299	0.1515	0.5299

ly compensated by the large increases in the $M(d_{xz}, d_{xy})$—$C_1(p_y)$ bond indices. The most important influences on the bonding in π-$C_3H_5Co(CO)_3$ as τ increases are therefore the increasing participation of the p_y orbitals of the terminal carbon atoms and the metal d_{xy} orbitals. The results of the calculations indicate (Table 4) that the τ angle of 36° of π-$C_3H_5Co(CO)_3$ is caused by the increased participation of the $C_1(p_y)$ and $M(d_{xy})$ orbitals which offset the diminished participation of the $C_1(p_z)$ orbitals.

Variation of the τ angle of π-$C_3H_5Ni(\pi$-$C_5H_5)$ through 0°, 18°, 30°, 40° (Table 3) yields a maximum M—C_1 bond index when τ = 18°, the experimentally observed τ tilt angle. The $M(d_{xy})$ orbital has an insignificant effect on the π-allyl—metal bonding (Table 5). The increase in the $M(d_{yz})$—$C_1(p_y)$ bond index from τ = 0° to τ = 18° is greater than the decrease in the $M(d_{xz})$—$C_1(p_z)$ bond index, but the accelerating decrease in the $M(d_{xz})$—$C_1(p_z)$ bonding is not matched by a similar increase in the $M(d_{xz})$—$C_1(p_y)$ bonding over the range τ = 18° to τ = 40°.

The results of the calculations therefore show that the τ tilting of the π-allyl group, like the bending of ring substituents out of the ring plane [34], is a consequence, at least in part, of interaction between the metal orbitals and part of the σ-framework of the ligand.

(ii) The ϕ angle of tilt. The calculated bond indices of π-$C_3H_5Co(CO)_3$ and π-$C_3H_5Ni(\pi$-$C_5H_5)$ (Table 1) show that the central carbon atom is considerably more weakly bonded to the metal atom than the terminal carbon atoms, due principally to the non-involvement of the central carbon atom in the ψ_2 molecular orbital. The M—C_2 bond length, however, is shorter than the M—C_1 and M—C_3 bond lengths.

TABLE 3

VARIATIONS OF M—C(π-allyl) BOND INDICES WITH τ AND ϕ IN π-$C_3H_5Ni(\pi$-$C_5H_5)$

ϕ (°)	τ (°)	M—C_1	M—C_2	M—C_3
103.16	0	0.4430	0.1877	0.4430
	18	0.4474	0.1961	0.4474
	30	0.4411	0.2048	0.4411
	40	0.4264	0.2098	0.4264
90		0.4450	0.2607	0.4450
150		0.4155	0.1039	0.4155

TABLE 4

VARIATIONS OF M(d_{xz}, d_{xy})—C$_1$(p_z, p_y) BOND INDICES WITH τ IN π-$C_3H_5Co(CO)_3$

τ (°)	M(d_{xz})—C$_1$(p_z)	M(d_{xz})—C$_1$(p_y)	M(d_{xy})—C$_1$(p_z)	M(d_{xy})—C$_1$(p_y)
0	0.3403	0.0005	0.0041	0.0001
10	0.3362	0.0062	0.0149	0.0010
20	0.2993	0.0303	0.0337	0.0055
36	0.2009	0.0879	0.0559	0.0319
60	0.0581	0.1363	0.0456	0.1359

If the terminal carbon atoms of π-$C_3H_5Co(CO)_3$ are in the xz-plane and $\phi = 90°$, the M—C$_2$ bond index is considerably greater than that when $\phi = 105°$, whereas the M—C$_1$ bond index decreases (Table 2). If the terminal carbon atoms are fixed in their known positions and ϕ is varied through 105° and 150° the M—C$_2$ bond index decreases, whereas the M—C$_1$ bond index is at a maximum when $\phi = 105°$. The experimental values of ϕ in π-$C_3H_5Co(CO)_3$ and π-C_3H_5-Ni(π-C_5H_5) are 105° and 103.16°, respectively. When the M—C$_2$ bond index is relatively high and the M—C$_1$ bond index relatively low an imbalance is created in the contributions of the central and terminal carbon atoms to the bonding orbital, ψ_1. The C$_1$ and C$_2$ contributions to the bonding of the ψ_1 orbital to the metal atom depend on the magnitude of the ϕ angle. When the ϕ angle is such that C$_2$ contributes more to the bonding of the ψ_1 orbital to the metal atom than C$_1$ by a factor of ca. $\sqrt{2}$, then ψ_1—M bonding is balanced and ϕ is ca. 105° for both compounds. The ϕ angle of 105° can readily be shown to give an M—C$_2$ bond length of ca. 2.0 Å given the M—C$_2$ (2.10 Å) and C—C (1.41 Å) bond lengths and the C—C—C (120°) bond angle.

B. Effects of the π-allyl group

The effects of the π-allyl group on other groups bonded to the metal atom are caused by the electronic nature, the tilting, and in some cases [7, 8], the steric effect of the π-allyl group.

(i) Asymmetric bonding. The bond indices of the M—C(O) groups of π-$C_3H_5Co(CO)_3$ are given in Table 6. The carbonyl group *cis* to the π-allyl group (Fig. 1) is more weakly bonded to the metal atom than the *trans* carbonyl groups because of two possible factors: the electronic nature and the tilt (or position) of the π-allyl group.

The π-allyl group causes the same CO group to be more weakly bonded to the metal atom in the τ-angle range 0° to 60° (Table 6). When $\tau = 0°$ the π-allyl group is *trans* to the labile CO group (Fig. 2). The cause of the lability of the

TABLE 5

VARIATIONS OF M(d_{xz}, d_{xy})—C$_1$(p_z, p_y) BOND INDICES WITH τ IN π-C_3H_5Ni(π-C_5H_5)

τ (°)	M(d_{xz})—C$_1$(p_z)	M(d_{xz})—C$_1$(p_y)	M(d_{xy})—C$_1$(p_z)	M(d_{xy})—C$_1$(p_y)
0	0.2154	0.0002	0.0073	0
18	0.2114	0.0162	0.0000	0
30	0.1742	0.0446	0.0035	0.0009
40	0.1302	0.0692	0.0087	0.0046

TABLE 6

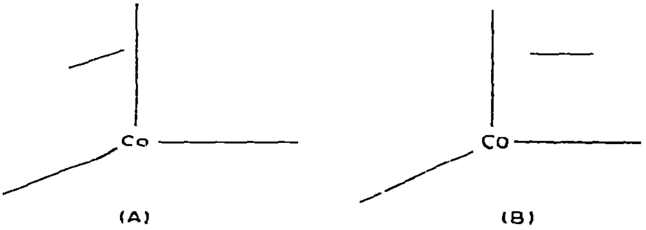
VARIATIONS OF M—C(O) BOND INDICES WITH τ IN π-$C_3H_5Co(CO)_3$

τ (°)	M—C_1(O)	M—C_2(O)	M—C_3(O)
0	0.5175	0.4668	0.5175
10	0.5184	0.4522	0.5184
20	0.5210	0.4355	0.5210
36	0.5268	0.4069	0.5268
60	0.5397	0.3629	0.5397
Symmetrical $M(CO)_3$ OC—M—CO = 103° τ = 36°	0.5363	0.3719	0.5363

unique carbonyl group is the electron donation by the ψ_2 orbital to the metal d_{xz} orbital which has the most significant influence (of the d orbitals) on the bonding of the *trans*-CO groups, but is almost uninvolved in the bonding of the *cis*-CO group. Even when the π-allyl group is *trans* to the unique CO group (τ = 0°) there is substantial donation by the ψ_2 orbital to the M(d_{xz}) orbital and consequently to the two remaining M—C(O) groups. The primary cause of the weak bonding of one CO group is therefore the electronic nature of the π-allyl group.

The effect of the tilting of the π-allyl group on the asymmetry of the $M(CO)_3$ bonding can be measured by the variations in bond indices with the τ angle of tilt (Table 6). The asymmetry of the $M(CO)_3$ group increases with increasing τ, the *cis*-M—C(O) bond becoming weaker and the *trans*-M—C(O) bonds becoming stronger. The asymmetry of the $M(CO)_3$ group, caused primarily by the electronic effect of the π allyl group, is approximately doubled by the 36° τ angle of tilt of the π-allyl group in π-$C_3H_5Co(CO)_3$.

Asymmetric bonding has been observed in the π-cyclopentadienyl group of $[\pi$-$C_3H_4Ni(\pi$-$C_5H_5)]_2$ [11] in which the π-cyclopentadienyl group has a π-allyl-type grouping and a C—C bond which has more double bond character than the other C—C bonds in the moiety. The calculations on π-$C_3H_5Ni(\pi$-$C_5H_5)$, with equal C—C bond lengths in the π-C_5H_5 moiety, show that the M—C and C—C bond indices are not equal (Table 7), primarily because of the asymmetry of the electronic field of the metal atom caused by the donation of the π-allyl C(p_z) orbitals to the metal d_{xz} orbital, and because of the geometrical distribution of the carbon atoms of the π-cyclopentadienyl group. The contribution to the asymmetric Ni—(π-C_5H_5) bonding of the 18° tilting of the π-C_3H_5 group is



(A) (B)

Fig. 2. Distribution of the π-C_3H_5-Co group when τ = 36° (A) and τ = 0° (B).

TABLE 7

VARIATIONS OF M–C(π-C_5H_5) AND C–C(π-C_5H_5) BOND INDICES WITH τ IN π-$C_3H_5Ni(\pi$-$C_5H_5)$

τ (°)	M–C_1	M–C_2	M–C_3	M–C_4	M–C_5	C–C
0	0.2466	0.1589	0.2446	0.2231	0.2231	1.3339, 1.3339, 1.2065, 1.1085, 1.2065
18	0.2511	0.1752	0.2541	0.2085	0.2085	1.3276, 1.3276, 1.2098, 1.4135, 1.2098
30	0.2564	0.1836	0.2564	0.1962	0.1962	1.3241, 1.3241, 1.2109, 1.4178, 1.2109
40	0.2546	0.1891	0.2546	0.1830	0.1830	1.3214, 1.3214, 1.2114, 1.4211, 1.2114

TABLE 8

CARBONYL FREQUENCIES, FORCE CONSTANTS, REACTION MECHANISMS AND RATE CONSTANTS OF π-$C_3H_5Co(CO)_3$, π-$C_3H_5Fe(CO)_2NO$, $Co(NO)(CO)_3$ AND $Ni(CO)_4$ [IN REACTION WITH $P(C_6H_5)_3$]

Compound	ν(CO)(cm^{-1})	k(CO) (md Å^{-1})	Reaction mechanism	Rate constant	Ref.
π-$C_3H_5Co(CO)_3$	2068, 2000 [a]	16.53	Dissociative	1.14×10^{-2} sec^{-1} [d]	35
π-$C_3H_5Fe(CO)_2NO$	2031, 1984 [b]	16.31	Associative	1.00×10^{-4} l m^{-1} sec^{-1} [e]	36
$Co(NO)(CO)_3$	2110, 2042 [b]	17.23	Associative	1.10×10^{-3} l m^{-1} sec^{-1} [f]	38
$Ni(CO)_4$	2116, 2046 [c] [$Ni(CO)_3(C^{18}O)$]	17.30	Dissociative	2.03×10^{-2} sec^{-1} [g]	39

[a] Ref. 6, cyclohexane solution. [b] Toluene solution. [c] n-Hexane solution. [d] Ether solution at 25°, [L] = 0.063 *M*, [S] = 0.072 *M*. [e] Toluene solution at 50°, [L] = 1.0 mol l^{-1}. [f] Toluene solution at 25°, [L] = 0.993 mol l^{-1}. [g] Toluene solution at 25°, [L] in the range 0.005—0.5 *M*. Concentration of substrate in each of *e*, *f* and *g* = *ca* 10^{-3} *M*

approximately equal to that due solely to the electronic effect of the π-allyl group.

(ii) Reactivity of π-$C_3H_5Co(CO)_3$. π-$C_3H_5Co(CO)_3$ reacts rapidly with $P(C_6H_5)_3$ in a reaction which is first-order in concentration of substrate and zero-order in concentration of ligand when the ligand concentration is greater than 0.06 *M* [35], and the kinetic data indicate that the reaction is dissociative. The reaction of π-$C_3H_5Fe(CO)_2NO$ with $P(C_6H_5)_3$ is first-order in concentration of substrate and first-order in concentration of ligand [36], indicating an associative reaction mechanism, and the reaction is considerably slower than that of π-$C_3H_5Co(CO)_3$ (Table 8). The results suggest that π-$C_3H_5Co(CO)_3$ reacts by breakage of a M—C(O) bond in the rate-determining step, whereas the reaction of π-$C_3H_5Fe(CO)_2NO$ is bimolecular and does not proceed initially by bond breakage. $Co(NO)(CO)_3$ reacts with $P(C_6H_5)_3$ with predominantly second-order kinetics and a small first-order contribution [37, 38], while $Ni(CO)_4$ reacts by dissociation [39]. Metal carbonyl compounds can be predisposed to first-order kinetics by the lability of one or more M—C(O) bonds, while relatively strong M—C(O) bonds can be expected to be conducive to non-dissociative reaction paths.

The infrared carbonyl stretching frequencies [ν(CO)] of the series π-C_3H_5-$Co(CO)_3$, π-$C_3H_5Fe(CO)_2NO$, $Co(NO)(CO)_3$ and $Ni(CO)_4$ are shown in Table 8. π-$C_3H_5Co(CO)_3$ occupies an apparently anomalous position among the Cotton—Kraihanzel [40] carbonyl force constants [*k*(CO)], because *k*(CO) of π-C_3H_5-$Co(CO)_3$ empirically suggests that the M—C(O) bonds are relatively strong.

The calculated M—C(O) bond indices for the series of compounds are shown in Table 9. The average M—CO bond order of π-$C_3H_5Co(CO)_3$ is considerably lower than those of π-$C_3H_5Fe(CO)_2NO$ and $Co(NO)(CO)_3$ but is nearly equal to that of $Ni(CO)_4$, and a carbonyl ligand should most easily dissociate from π-$C_3H_5Co(CO)_3$ and $Ni(CO)_4$. The results therefore indicate that the anomalously high reactivity of π-$C_3H_5Co(CO)_3$ is caused by the combined electronic effect and tilting of the π-allyl group.

(iii) Reactivity of π-$C_3H_4RCo(CO)_3$ ($R = H$, 1-CH_3, 1-Cl, 2-CH_3, 2-Cl) The relative rates of reactions of the compounds π-$C_3H_4RCo(CO)_3$ (R = H, 1-CH_3, 1-Cl, 2-CH_3, 2-Cl) with $P(C_6H_5)_3$ are in order 1-Cl < 1-CH_3 < H < 2-CH_3 < 2-Cl [35], whereas the compounds π-$C_3H_4RFe(CO)_2NO$ react with the relative rates 1-CH_3, 2-CH_3 < H < 1-Cl, 2-Cl [41], and the M—C(O) groups *trans* to the π-allyl ligand in the iron compound therefore experience the normal substituent effects. The essential difference between the two sets of compounds is the occupation of the NO site in one compound by a labile CO group in the other. The unusual kinetic substituent effects in the cobalt compounds must therefore be

TABLE 9

M—C(O) AND C—O BOND INDICES OF π-$C_3H_5Co(CO)_3$, π-$C_3H_5Fe(CO)_2NO$, $Co(NO)(CO)_3$ AND $Ni(CO)_4$

Compound	M—C(O)(ave.)	C—O (ave.)
π-$C_3H_5Co(CO)_3$	0.4868	2.4467
π-$C_3H_5Fe(CO)_2NO$	0.5689	2.4375
$Co(NO)(CO)_3$	0 5473	2 4967
$Ni(CO)_4$	0.4810	2.5210

TABLE 10

M—C(O) AND C—O BOND INDICES OF π-$C_3H_4RCo(CO)_3$ (R = H, 1-CH_3, 1-Cl, 2-CH_3, 2-Cl)

R	M—C(O)			C—O		
H	0.5268	0.4069	0.5268	2.4541	2.4318	2.4541
1-CH_3	0.5072	0.4068	0.5079	2.4499	2.4253	2.4500
1-Cl	0.4987	0.4101	0.5294	2.4579	2.4409	2.4604
2-CH_3	0.5268	0.4020	0.5268	2.4524	2.4292	2.4524
2-Cl	0.5279	0.4014	0.5279	2.4628	2.4392	2.4628

caused by the substituent effects on the unique, labile M—C(O) group. Calculations on π-$C_3H_4RCo(CO)_3$ (R = H, 1-CH_3, 1-Cl, 2-CH_3, 2-Cl) show that the unique M—C(O) bond indices correlate with the kinetic rate constants, although the normal substituent effects are reflected in the other M—C(O) bond indices (Table 10).

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