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Carbon-13 Nuclear Magnetic Resonance Spectra of (olefin)Ni[P(O-*o*-tol)$_3$]$_2$ Complexes

C. A. TOLMAN,* A. D. ENGLISH, and L. E. MANZER

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Carbon-13 NMR chemical shifts and C–H coupling constants are reported for a series of (olefin)Ni[P(O-*o*-tol)$_3$]$_2$ (tol = tolyl) complexes where olefin = ethylene, acrylonitrile, fumaronitrile, methyl acrylate, dimethyl maleate, and maleic anhydride. ^{1}H NMR data and preparations of the new complexes of fumaronitrile, methyl acrylate, and dimethyl maleate are described. The relationship between ^{13}C and ^{1}H data and metal–olefin bonding is discussed.

Introduction

Recent years have seen a rapid growth in the application of ^{13}C NMR to bonding and structure studies in organometallic chemistry. Because of our interest in olefin complexes of Ni(0),[1-3] we wanted to see what could be learned from ^{13}C in a series of (olefin)NiL$_2$ complexes where L = P(O-*o*-tol)$_3$. They have already been thoroughly studied by a variety of other spectroscopic methods including ^{1}H and ^{31}P NMR, ir, optical spectroscopy, and ESCA.[4] Single-crystal X-ray studies have been done on the ethylene and acrylonitrile complexes.[5] Our interest was increased by the controversy[6a,7] over the relationship between ^{13}C coordination chemical shifts and π back-bonding in other complexes.

We report here ^{13}C NMR studies on coordinated and free olefins—ethylene, acrylonitrile (ACN), fumaronitrile (FMN), methyl acrylate (MAC), dimethyl maleate (DMM), and maleic anhydride (MA)—and discuss both chemical shifts and C–H coupling constants. To our knowledge only three other ^{13}C NMR studies of functionally substituted olefin complexes have appeared.[8] We also give ^{1}H NMR data on the complexes and discuss the relationship between ^{1}H and ^{13}C NMR chemical shifts.

Results

^{13}C resonances were readily assigned on the basis of undecoupled spectra. Figure 1 shows the high-field region of the methyl acrylate complex (MAC)NiL$_2$. The triplet of doublets (a), doublet of doublets (b), and quartet (c) are clearly assigned to the CH$_2$=, =CH–, and –CH$_3$ carbons of the coordinated olefin. The small splittings of 23 Hz in (a) and 17 Hz in (b) are assigned to $J(\text{P–C})_{\text{trans}}$ in each case; presumably $J(\text{P–C})_{\text{cis}}$ is very small. The two different couplings are consistent with the near-planar arrangement of the heavy atoms found in the structure of the acrylonitrile complex.[5]

Carbon–phosphorus coupling was also seen in the DMM and MA complexes. Olefinic carbons of the DMM complex showed virtual coupling and appeared as a 1:1:1 triplet (outside spacing $|J_{\text{CP}} + J_{\text{CP'}}| = 23$ Hz) in the proton-decoupled spectrum. Carbons of the MA complex appeared as a doublet with a 24-Hz spacing with a small line in the center. The patterns indicate that $J_{\text{PP'}}$ is smaller for the MA complex.

Carbon–phosphorus coupling was not resolved in the ethylene or cyanoolefin spectra, possibly because of rapid intermolecular exchange. The carbon resonances of these coordinated olefins were typically ~40 Hz wide.

^{13}C NMR Chemical Shifts. Table I shows that $\Delta\delta$(C), the upfield shift of carbons on coordination, is uniformly large (75–95 ppm) for the double-bond carbons and increases with substitution of H by electronegative groups. Comparing chemical shifts of coordinated olefins ($\delta(\text{C}_{\text{coord}})$) shows that the CH$_2$= carbons of MAC or ACN are ~4 ppm to high field of ethylene. Coordinated =CH– carbons are ~4 ppm to low field in MAC or DMM and ~21 ppm to higher field in ACN and FMN.

The –CO$_2$– carbons, which are farthest downfield in the free olefins, are shifted to lower field on coordination, ~6 ppm. The ester methyl resonances, as expected, are not affected much by coordination. Nitrile carbons gave very weak resonances in the free cyanoolefin spectra and were obscured by the aromatic ligand carbons in the complexes.

C–H Coupling Constants. Values of ^1J(C–H) in the free olefins (Table I) show the usual[9a] increase in carbon s character caused by electronegative substitution. On this basis the olefins can be ranked in order of increasing substituent electronegativity: C$_2$H$_4$ (157) < MAC (170) ~ DMM (168) < ACN (182) ~ FMN (184) < MA (188). The unsubstituted carbons of MAC (162) and ACN (166) also show the effect of substitution but to a lesser extent. ^1J(C–H) is reduced on coordination to the ~160 Hz of coordinated ethylene for all olefinic carbons except for =CH– of ACN and FMN, which are reduced only to ~175 Hz.

Ester methyl ^1J(C–H) of ~146 Hz is typical for esters and is unaffected by coordination.

^{1}H NMR Spectra. Data on the free olefins and complexes are shown in Table II. Olefinic proton resonances shift upfield on coordination by 1.75–4.01 ppm. The proton shifts reflect the ^{13}C shifts in the sense that H$_a$ and H$_b$ shift more than H$_c$. The shift series C$_2$H$_4$ > DMM > MAC is however the reverse of the ^{13}C series.

The ^{1}H spectrum of the MAC complex was unique in showing two types of phosphite in a 1:1 ratio (ortho H doublets (J = 8 Hz) at τ 3.41 and 3.52; ortho CH$_3$ singlets at τ 7.77 and 7.98) due to L cis or trans to the ester group. The olefinic hydrogens appeared as complex multiplets with both H–H and P–H coupling and were assigned by analogy with (ACN)NiL$_2$.[2]

Discussion

Equilibrium constants of olefin complex formation (eq 1)

$$\text{olefin} + \text{NiL}_3 \overset{K}{\rightleftharpoons} (\text{olefin})\text{NiL}_2 + \text{L} \qquad (1)$$

for L = P(O-*o*-tol)$_3$ show an increase in the series C$_2$H$_4$ < MAC < DMM ~ ACN < FMN ~ MA from 2.5×10^2 to 4.0×10^8 (benzene, 25°).[3] Increasing back-donation from nickel to olefin π^* orbitals in the series is indicated by electronic[2,3] and ESCA[4] spectra of the complexes. Figure 2 shows the relationships between $\Delta\delta$(C) and log K. The rather good correlations for unsubstituted (open circles) and substituted carbons (closed circles) indicates that increased back-bonding from nickel to olefin π^* orbitals is associated with a larger shift to high field. The very large $\Delta\delta$(C) of the unsubstituted carbons of ACN and MAC can be understood in terms of two contributing effects: (1) the low-field position of the unsubstituted carbons (15 and 7 ppm below C$_2$H$_4$) in the free olefins, arising from a resonance interaction of the substituents[9b] (this resonance is destroyed on coordination to the metal); (2) the effect of metal π back-bonding, which may be roughly the same to both carbons or even slightly higher to the substituted carbon.[9c]

Clark and coworkers[6a] suggested a relationship between π

Table I. ^{13}C Data[a] for Olefins and (olefin)Ni[P(O-*o*-tolyl)$_3$]$_2$ Complexes

Olefin	$\delta(C_{free})$	$\delta(C_{coord})$	$\Delta\delta(C)^b$	$^1J(C-H)_{free}$	$^1J(C-H)_{coord}$
Ethylene					
$H_2C=$	122.8	47.4	75.4	157	160 ± 5
Acrylonitrile[c]					
$H_2C=$	137.8	42.7	95.1	166	165 ± 5
=CH-	108.2	25.9	82.3	182	175 ± 5
-CN	117.5	*e*			
Fumaronitrile[c]					
=CH-	117.8	24.8	93.0	184	172 ± 5
-CN	114.1	*e*			
Methyl acrylate					
$CH_2=$	129.9	44.7	85.2	162	156^f
=CH-	128.5	52.4	76.1	170	160^g
$-CO_2-$	166.0	172.5	−6.5		
$-CH_3$	50.8	50.2	0.6	146	146
Dimethyl maleate					
=CH-	130.0	51.1	78.9	168	160^h
$-CO_2-$	165.6	170.7	−5.1		
$-CH_3$	51.6	49.6	2.0	148	146
Maleic anhydride[d]					
=CH-	137.1	47.8	89.3	188	160^i
$-CO_2-$	165.0	*e*			

[a] Chemical shifts of carbons in free and coordinated olefins in ppm (±0.1) downfield of TMS. The uncertainty in $^1J(C-H)$ is ±2 Hz except where noted otherwise. [b] Positive values of $\Delta\delta(C) = \delta(C_{free}) - \delta(C_{coord})$ indicate an upfield shift. [c] $^2J(C-H)$ values in the free olefin are 7 ± 1 Hz. [d] $^2J(C-H) = 4$ Hz. [e] Not observed. [f] $|J_{CP} + J_{CP'}| = 23$ Hz. [g] $|J_{CP} + J_{CP'}| = 17$ Hz. [h] $|J_{CP} + J_{CP'}| = 23$ Hz. [i] $|J_{CP} + J_{CP'}| = 24$ Hz.

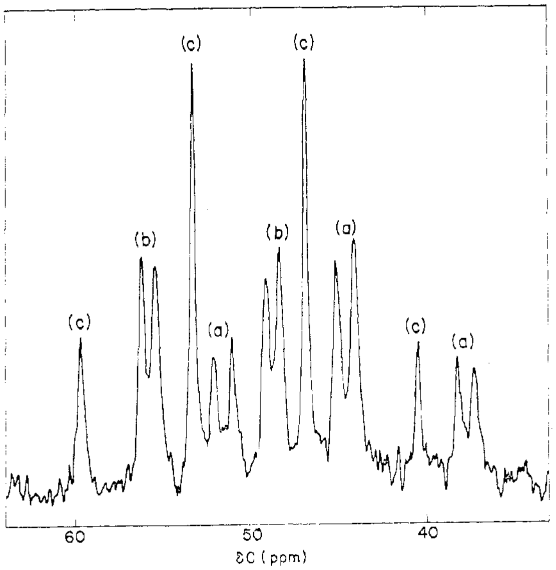
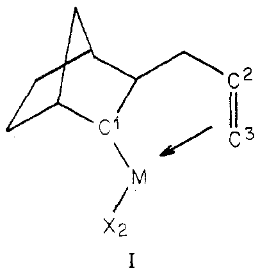
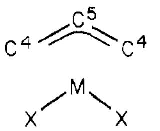


Figure 1. Undecoupled high-field region of the ^{13}C NMR spectrum of (MAC)Ni[P(O-*o*-tol)$_3$]$_2$ in C_6D_6: (a) $CH_2=$; (b) =CH−; (c) $-CH_3$.

back-bonding and ^{13}C coordination shifts. Increasing $\Delta\delta(C)$ was observed in the order $[CH_3Pt(C_2H_4)(PMe_2Ph)]^+ < [(C_2H_4)PtCl_3]^- < (C_2H_4)Pt(PPh_3)_2$ and $(COD)Pt(CF_3)_2 < (COD)Pt(CH_3)_2$, where COD = 1,5-cyclooctadiene. This relationship was questioned by Powell and coworkers[7] on the basis of results on compounds of types I and II [M = Pd, Pt;



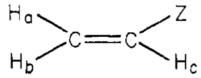
I



II

X_2 = hexafluoroacetylacetonate (hfacac) or X = Cl, Br, I (dimers)]. Resonances of carbons 1–4 moved to high field in the order I < Br < Cl < hfacac and Pd(II) < Pt(II). Good correlations of $\delta(C^2)$, $\delta(C^3)$, and $\delta(C^4)$ with $\delta(C^1)$ and larger changes in $\delta(C^1)$ were observed. This and the similarity of changes in $\delta(C^1)$ and $\delta(H)$ in *trans*-$[HMX(PEt_3)_2]$ complexes led the authors to suggest that changes in chemical shifts are primarily due to a change in a nonbonding shielding term associated with partly filled d orbitals, rather than to changes in metal–carbon bonding. The nonbonded shielding theory is inadequate because it predicts small upfield shifts for metals with filled d orbitals. Larger $\Delta\delta(C)$ values are observed for platinum(0)–olefin complexes than for Pt(II) complexes.[6] Our Ni(0) complexes (also d^{10} systems) show even larger upfield shifts. A similar close relationship between $\Delta\delta(C)$ of σ-bonded carbons and π-bonded carbons has been reported more recently by Clark and coworkers[6b] in a series of $CH_3Pt(COD)L^+$ complexes (where L is Cl^- or a variety of neutral Lewis bases). Clark concluded that "any π-bonding component reflected in

Table II. ^1H Data for Olefins and (olefin)Ni[P(O-*o*-tol)$_3$]$_2$



Olefin	τ_{free}	τ_{coord}	$\Delta\tau$		^3J-(P–H)$_{coord}$
Ethylene[a]	4.76	8.06	3.30		*i*
Acrylonitrile[b]					*i*
H_a	4.71^g	8.72^h	4.01		
H_b	5.08	8.83	3.75	3.17^f	
H_c	5.36	7.11	1.75		
Fumaronitrile	5.51	1.82	3.69		*i*
Methyl acrylate					
H_a	3.70	7.22	3.52		*c*
H_b	4.72	8.20	3.48	3.31^f	*c*
H_c	4.06	6.98	2.92		*c*
$-CH_3$	6.64	6.87	0.23		
Dimethyl maleate					
=CH−	4.19	6.95	2.76		3^d
$-CH_3$	6.56	6.85	0.29		
Maleic anhydride	4.50	7.00	2.50		3^e

[a] Data from ref 1. [b] Data from ref 2. [c] Complex multiplets. [d] Doublet. [e] Triplet. [f] Mean value. [g] $J_{ac} = 17$ Hz, $J_{bc} = 12$ Hz, $J_{ab} = 2$ Hz. [h] $J_{ac} = 13$ Hz, $J_{bc} = 10$ Hz, $J_{ac} = 3$ Hz. [i] Not observed.

Table III. $\Delta\delta$(C)[a] of Substituted Ethylene Complexes of Other Metals

	CH_2=	=CH–
$(CH_2{=}CHCN)Ag^+$	–4.4	+1.6
$(CH_2{=}CHCH_2CN)Ag^+$	+0.3	+1.9
$(CH_2{=}CHC_4H_9)Ag^+$	+13.7	+3.2
$(CH_2{=}CHOCH_2CH_3)Ag^+$	+18.1	–4.4
$(CH_2{=}CHCOOCH_2CH_3)Fe(CO)_4$	+95.7[c]	+84.6
$(CH_2{=}CHCOOCH_2CH_3)Ru(CO)_4$	+105.7[c]	+92.4
(DEF)$Fe(CO)_4$[b]		+89.1
(DEF)$Ru(CO)_4$		+96.4

[a] Data on Ag^+ complexes from ref 8a and on Fe(0) and Ru(0) from ref 8c. Positive values mean a shift to high field on coordination. [b] DEF represents diethyl fumarate. [c] Revised values from J. Takats, private communication.

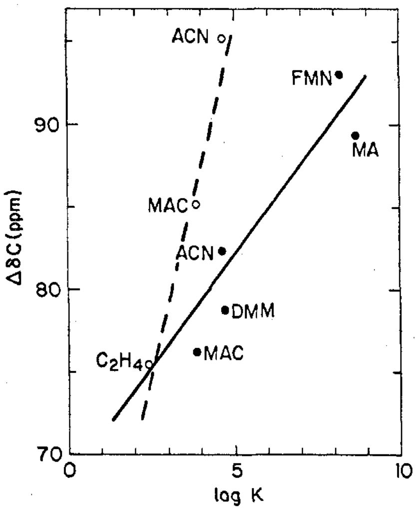


Figure 2. Upfield shift of olefinic carbons on coordination to form (olefin)$Ni[P(O\text{-}o\text{-}tol)_3]_2$ plotted against log *K* from ref 3 for the reaction olefin + $NiL_3 \rightleftharpoons$ (olefin)NiL_2 + L. Open circles refer to CH_2= and closed to =CH–.

the olefinic shieldings...either remains fairly constant or changes parallel to the changes in σ-inductive and neighbor anisotropy effects" and favors the former.

In our system, where there are no σ-bonded carbons, there is a clear relationship between π back-bonding and $\Delta\delta$(C) of the olefinic carbons. The close relationship between the behavior of σ- and π-bonded carbons in other systems[6b,7] leads us to conclude that the factors which make for good π back-bonding to olefins (high metal electron density, low trans influence of a trans ligand) also give increased shielding of σ-bonded carbons.

Going from ethylene to propylene in (olefin)$_2$Rh(acac) complexes (acac = acetylacetonate) reduces $\Delta\delta$(C) of the double-bond carbons from 85.8[10] to a mean of 57.6 ppm.[11] This reduction is consistent with reduced π back-bonding in the propylene complex.

Salomon and Kochi[13] measured $\Delta\delta$(C) and $\Delta\delta$(H) in a series of (cyclic olefin)copper(I) CF_3SO_3 complexes. They found that olefins whose protons shift farther upfield on coordination show larger upfield shifts of their carbons and concluded that both parameters reflect the degree of Cu→olefin back-bonding.

Table III shows literature values of $\Delta\delta$(C) for some substituted ethylene complexes of other metals. Ag^+, expected to be poor at π back-bonding, shows *increasing* positive $\Delta\delta$(C) of CH_2= as the substituents become better resonance donors. This behavior is opposite to Ni(0). The shifts are all relatively small. Fe(0) and Ru(0), much better donors, give large positive shifts. On the basis of $\Delta\delta$(C)'s for these ethyl acrylate complexes[14] and our values for methyl acrylate, we assign an order of back-bonding ability $Ru(CO)_4 > Fe(CO)_4 > Ni[P(O\text{-}o\text{-}tol)_3]_2$. Better back-bonding of Ru than of Fe is also consistent with higher activation energies for olefin rotation.[8c]

^{13}C and other types of spectroscopic data on a number of ethylene complexes are shown in Table IV. δ(C) covers a wide range; the large downfield shift of $(C_2H_4)Hg^{2+}$ is especially noteworthy. There is a rough correlation between δ(C), τ, and other measures of back-bonding, such as $\nu_{C=C}$ and $d_{C=C}$. There are difficulties, however. Greater back-bonding in $(C_2H_4)_2RhCp$ than in $(C_2H_4)_2Rh(acac)$ is suggested both by τ and $\nu_{C=C}$, while δ(C) goes the other way. More back-bonding in $(C_2H_4)Ni[P(O\text{-}o\text{-}tol)_3]_2$ than in $(C_2H_4)Pt(PPh_3)_2$ is suggested by τ and $\delta_{C=C}$ but not by δ(C).

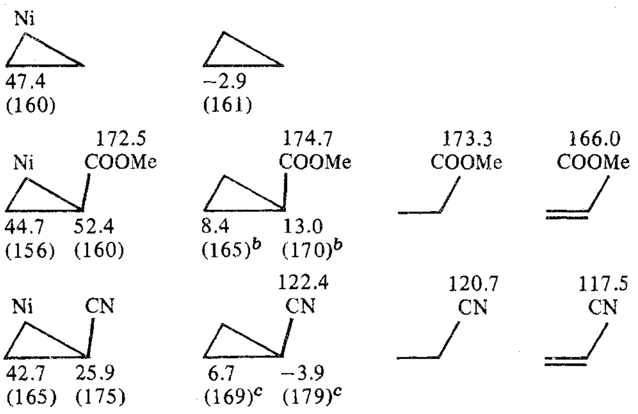
Values of ^1J(C–H) of ethylene complexes are usually near 160 Hz and show no correlation with other measures of back-bonding. This is perhaps not surprising, since ^1J(C–H) changes only 4 Hz on going from C_2H_4 to cyclopropane. (The

Table IV. ^1H and ^{13}C NMR, Ir, and Structural Data[a] on Cyclopropane and Ethylene Complexes

Compd	τ	$\nu_{C=C}$,[b] cm^{-1}	$d_{C=C}$, Å	δ(C)	^1J(C–H), Hz
Cyclopropane	9.8[c]	1470[d]	1.53[e]	–3.5[f]	161[f]
Ethylene oxide	7.2	1487	1.47	39.7[f]	176[g]
$(C_2H_4)(H)NbCp_2$[h]	8.9, 9.4			13.4, 8.0	153, 156
$(C_2H_4)(C_2H_5)NbCp_2$[h]	8.7, 9.1		1.41	29.4, 27.6	153, 154
$(C_2H_4)Ni[P(O\text{-}o\text{-}tol)_3]_2$	8.1	1487	1.46	47.4[i]	160[i]
$(C_2H_4)_2RhCp$	8.1[j]	1493[j]		61.2[k]	160[k]
$(C_2H_4)Ni(PCy_3)_2$	8.0[l]			37.7[l]	
$(C_2H_4)Pt(PPh_3)_2$	7.4		1.43	39.6[m]	146[n]
$(C_2H_4)Rh(acac)$	6.9	1524	1.41	37.5[k]	158[k]
$(C_2H_4)RhCl(PPh_3)_2$	5.6			44.6[o]	
$(C_2H_4)PtCl_3^-$	5.3	1526	1.35	75.1[p]	
$(C_2H_4)(CH_3)Pt(PMe_2Ph)_2^+$	5.9[q]			84.4[m]	
$(C_2H_4)Ag^+$	4.3	1583		[r]	
$(C_2H_4)Hg^{2+}$	2.3[s]			134.8[s]	
C_2H_4	4.7	1623	1.34	122.8[i]	157[i]

[a] From ref 2 unless noted otherwise. [b] This mode is mixed with the symmetric CH_2 scissoring vibration and is mostly scissoring near the top of the table. See the discussion in ref **2**. [c] K. B. Wiberg and B. J. Nist, *J. Am. Chem. Soc.*, 83, 1228 (1961). [d] Mean of ν_2 and ν_9 from G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules", Van Nostrand, Princeton, N.J., 1964, p 352. [e] *Chem. Soc., Spec. Publ.*, No. 11 M149 (1958). [f] J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972, pp 161, 270, and 336. [g] P. D. Ellis and G. E. Maciel, *J. Am. Chem. Soc.*, **92**, 5829 (1970). [h] L. J. Guggenberger, P. Meakin, and F. N. Tebbe, *J. Am. Chem. Soc.*, 96, 5420 (1974). [i] This work. [j] R. Cramer, *J. Am. Chem. Soc.*, 86, 217 (1964). [k] Reference 10. [l] C. A. Tolman, unpublished results. [m] Reference 6. [n] C. D. Cook and K. Y. Wan, *J. Am. Chem. Soc.*, **92**, 2595 (1970). [o] C. A. Tolman, P. Z. Meakin, D. L. Lindner, and J. P. Jesson, *ibid.*, **96**, 2762 (1974). [p] L. F. Farnell, E. W. Randall, and E. Rosenberg, *Chem. Commun.*, 1078 (1971). [q] M. H. Chisholm and H. C. Clark, *Inorg. Chem.*, **12**, 991 (1973). [r] A resonance shifted upfield from free ethylene by an unspecified but presumably small amount was reported by C. D. M. Beverwijk and J. P. C. M. van Dongen, *Tetrahedron Lett.*, 4291 (1972). [s] G. A. Olah and P. R. Clifford, *J. Am. Chem. Soc.*, **95**, 6067 (1973). δ(C) was converted from a CS_2 standard, 192.8 ppm.

Table V. Comparative ^{13}C Data^a



^{a} Chemical shifts (in ppm relative to TMS) and ^1J(C–H) (in parentheses in Hz) taken from J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972, pp 161, 270, 307, and 336 except for olefins and nickel–olefin complexes. ^{b} Coupling constants for cyclopropanecarboxylic acid. ^{c} P. H. Weiner and E. R. Malinowski, *J. Phys. Chem.*, **71**, 2791 (1967).

larger value for ethylene oxide is due to an electronegativity effect.) A number of authors[6,10] have suggested that a high degree of back-bonding should give sp^3 hybridization at carbon, with values of ^1J(C–H) approaching 125 Hz. This is clearly not correct. The small angles inside a three-membered ring lead to concentration of carbon s character in the C–H bonds and p character in the ring, as shown for cyclopropane by Weigert and Roberts from C–C coupling data.[15]

Table V compares our ^{13}C data with those of some model hydrocarbons. ^1J(C–H) values are smaller for NiL_2 than for CH_2 in cyclopropane rings, indicating that NiL_2 is more effective in neutralizing the effect of electronegative substituents. Ring δ(C)'s are larger in the nickel complexes but approach the cyclopropane analogs for more electronegative substituents; the pattern of shifts is similar. Ester carbonyl δ(C)'s increase in the order of R = $CH_2{=}CH < CH_3CH_2$ < cyclopropyl. The value for (MAC)NiL_2 is closest to that of methyl propionate.

Although the cyclopropane model for strong back-bonding is attractive in some ways, it is deficient in two respects we have mentioned before.[3] Coupling constants J(H–H) in (ACN)Ni[P(O-*o*-tol)$_3$]$_2$[2] or a series of $(CH_2{=}CHZ)Fe(CO)_4$ complexes (Z = COOH, $COOCH_3$, or $CONH_2$)[16] are closer to the free olefin values than to those of cyclopropane models. Stretching frequencies $\nu_{C=O}$ or ν_{CN} in RCOOMe or RCN increase in the order R = $CH_2{=}CH < CH_3CH_2$ < cyclopropyl but are *lower* in the olefin complexes than in the free olefins.

Experimental Section

^{13}C NMR spectra were obtained on a Bruker HFX90–Digilab FTS/NMR-3 system. The spectra were obtained with both broad-band and gated proton decoupling. Chemical shifts were measured relative to the solvent and then adjusted to a tetramethylsilane (TMS) scale using $\delta_{C_6D_6}$ 128.0 ppm and $\delta_{CD_2Cl_2}$ 53.6 ppm.

Spectra were recorded at room temperature in CD_2Cl_2 except for (ACN)Ni[P(O-*o*-tol)$_3$]$_2$ at −30°. The lower temperature was used to freeze out exchange between complexed ligand and free ligand impurity. ^1H spectra were recorded on Varian 60-, 100-, and 220-Mz machines at ambient temperature in C_6D_6. Chemical shifts were measured with internal TMS.

Reactions and manipulations were performed under an atmosphere of dry nitrogen. Solvents were dried by passage through a column of Linde 4A molecular sieves and sparged with nitrogen prior to use. $(C_2H_4)NiL_2$ was prepared as described earlier.[1]

(Methyl acrylate)[bis(tri-*o*-tolyl phosphite)]nickel. Methyl acrylate (0.34 g, 3.79 mmol) was added to a stirred solution of $(C_2H_4)NiL_2$ (3.0 g, 3.79 mmol) in 25 ml of toluene. The solution was stirred for 1 hr, and the toluene was removed by rotary evaporation to give a yellow oil. The oil was dissolved in ether, pentane was added, and the solution was cooled to −40° overnight. The yellow crystals that separated were filtered off and dried under vacuum. The yield was 2.80 g; mp 76–80°.

Anal. Calcd for $C_{46}H_{48}NiO_8P_2$: C, 65.03; H, 5.69; O, 15.07. Found: C, 64.54; H, 5.89; O, 14.67.

(Fumaronitrile)[bis(tri-*o*-tolyl phosphite)]nickel. To a stirred solution of $(C_2H_4)NiL_2$ (3.0 g, 3.79 mmol) in 5 ml of toluene was added a solution of fumaronitrile (0.89 g) in toluene. The solution turned dark orange and ethylene was bubbled off. The addition was completed, the solution was filtered, and methanol was added. The color lightened, and after cooling to −30° overnight yellow crystals separated. They were filtered off and dried. The yield was 3.10 g; mp 142–144°.

Anal. Calcd for $C_{46}H_{44}N_2O_6P_2Ni$: C, 65.65; H, 5.27; O, 11.41; N, 3.33. Found: C, 66.47; H, 5.49; O, 11.16; N, 3.32.

(Dimethyl maleate)[bis(tri-*o*-tolyl phosphite)]nickel. To a stirred solution of $(C_2H_4)NiL_2$ (3.0 g, 3.80 mmol) in toluene was added dimethyl maleate (0.55 g). After 10 min of stirring, the solution was filtered and methanol was added. The solution was cooled to −40° for 12 hr. Pale yellow crystals separated. They were filtered off and dried; yield 3.20 g; mp 129–132°.

Anal. Calcd for $C_{48}H_{50}O_{10}P_2Ni$: C, 63.38; H, 5.76; O, 17.59. Found: C, 63.16; H, 5.72; O, 17.87.

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Registry No. C_2H_4, 74-85-1; (C_2H_4)Ni[P(O-*o*-tol)$_3$]$_2$, 31666-47-4; ACN, 107-13-1; (ACN)Ni[P(O-*o*-tol)$_3$]$_2$, 31666-48-5; FMN, 764-42-1; (FMN)Ni[P(O-*o*-tol)$_3$]$_2$, 53323-40-3; MAC, 96-33-3; (MAC)Ni[P(O-*o*-tol)$_3$]$_2$, 53323-42-5; DMM, 624-48-6; (DMM)-Ni[P(O-*o*-tol)$_3$]$_2$, 53323-41-4; MA, 108-31-6; (MA)Ni[P(O-*o*-tol)$_3$]$_2$, 41813-01-8; ^{13}C, 14762-74-4.

References and Notes

(1) W. C. Seidel and C. A. Tolman, *Inorg. Chem.*, **9**, 2354 (1970).
(2) C. A. Tolman and W. C. Seidel, *J. Am. Chem. Soc.*, **96**, 2774 (1974).
(3) C. A. Tolman, *J. Am. Chem. Soc.*, **96**, 2780 (1974).
(4) C. A. Tolman, W. M. Riggs, W. J. Linn, C. M. King, and R. C. Wendt, *Inorg. Chem.*, **12**, 2770 (1973).
(5) L. J. Guggenberger, *Inorg. Chem.*, **12**, 499 (1973).
(6) (a) M. H. Chisholm, H. C. Clark, L. E. Manzer, and J. B. Stothers, *J. Am. Chem. Soc.*, **94**, 5087 (1972); (b) M. H. Chisholm, H. C. Clark, L. E. Manzer, J. B. Stothers, and J. E. H. Ward, *ibid.*, **97**, 721 (1975).
(7) D. G. Cooper, R. P. Hughes, and J. Powell, *J. Am. Chem. Soc.*, **94**, 9244 (1972).
(8) (a) J. P. C. M. Van Dongen and C. D. M. Bevewijk, *J. Organomet. Chem.*, **51**, C36 (1973); (b) W. J. Cherwinski, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 1405 (1974); (c) L. Kruczynski, J. L. Martin, and J. Takats, *J. Organomet. Chem.*, **80**, C9 (1974).
(9) (a) H. A. Bent, *Chem. Rev.*, **61**, 275 (1961). (b) J. B. Stothers, "Carbon-13 Nmr Spectroscopy", Academic Press, New York, N.Y., 1972, pp 183–185. (c) The X-ray structure[5] of the ACN complex showed a shorter M–C bond distance to the substituted carbon (1.91 vs. 2.02 Å).
(10) G. M. Bodner, B. N. Storhoff, D. Doddrell, and L. J. Todd, *Chem. Commun.*, 1530 (1970).
(11) K. R. Aris, V. Aris, and J. M. Brown, *J. Organomet. Chem.*, C67 (1972), reported Δδ = 54.2[12] and 61.0 for $CH_2{=}$ and $={CH}–$, respectively.
(12) An average of resolved isomers.
(13) R. G. Salomon and J. K. Kochi, *J. Organomet. Chem.*, **64**, 135 (1974), **43**, C7 (1972).
(14) Reference 8c reported incorrect chemical shifts for the $CH_2{=}$ carbons. The correct values (J. Takats, private communication) are shown in Table III.
(15) F. J. Weigert and J. D. Roberts, *J. Am. Chem. Soc.*, **89**, 5926 (1967).
(16) E. Weiss, K. Stark, J. E. Lancaster, and H. D. Murdoch, *Helv. Chim. Acta*, **46**, 288 (1963).