to carbon shifts can be found in discussions of metal carbonyls. Various workers, most recently Bodner and Todd,[9] have proposed that the chemical shift of the carbonyl carbon atom is a linear measure of transition metal → carbonyl π back-donation. Available data[10,11] indicate that this linearity is only observed if the complexes are very closely related. Even $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ have chemical shifts of 212, 202, and 192 ppm, respectively. The suggestion[12] that the relationship applies to platinum carbonyl complex cations (where shifts of 19 ppm are observed with small changes (19 cm^{-1}) in ν_{CO}) is unlikely to be correct.

Another topic discussed from divergent viewpoints has been the shifts of π-bonded carbon atoms. One group[13] suggested that "nonbonded paramagnetic shielding effects" associated with partially filled metal d orbitals caused the upfield shift of π-bonded carbons upon coordination. The major evidence supporting this view was the observation of an approximately linear relationship between the shifts of π-bonded carbons and those of σ-bonded carbons in the same molecules. The proposal that slopes of $(R_{M-C_1}/R_{M-C_2})^3$ should be observed rested upon a misinterpretation of the theoretical work cited.[14,15] Finally the observation of only very small upfield shifts for olefins bound to d^{10} Ag(I)[16,17] is hardly a convincing argument for this shielding effect since ethylene bound to d^{10} Pt(0) in $PtL_2(C_2H_4)$ exhibits quite a marked upfield shift on complexation (+82.4 ppm),[18] as do olefins bound to Cu(I).[19]

Another group[18] suggested that the ^{13}C shifts in olefin complexes were due to changes in π-bond order resulting from metal–ligand π and π^* interactions: the metal only affects matters by altering the electron density in the various ligand molecular orbitals and hence the net bond orders within the original organic π system. If one quantifies this effect with the Pople "paramagnetic" term[20]

$$\sigma_{\mathrm{p}}{}^{\mathrm{AA}} = \frac{-e^2\hbar^2}{2m^2c^2(\Delta E)}\langle r^{-3}\rangle_{2\mathrm{p}}\Big(A_{\mathrm{AA}} + \sum_{\mathrm{B}\neq\mathrm{A}} Q_{\mathrm{AB}}\Big) \tag{3}$$

for any reasonable constant ΔE, the resulting simple calculations[21] show that such effects cannot by themselves account for the chemical shifts of carbon atoms π bonded to transition metals.

Two examples illustrate this clearly. First we consider π-cyclopentadienyl complexes. For any electron population reasonable in light of other physical measurements[22] and calculations,[23] shifts on complexation are calculated to be small (up to *ca.* 12 ppm for donation of 1.0 electron to the metal) and downfield of the resonance due to the free ligand. However, observed shifts for the complexed ligand vary over a considerable range, from 123.1 ppm for $C_5H_5TiCl_3$ to 63.9 ppm for $(C_5H_5)_2Os$.[24]

Second, the complexed π-allyl group also differs from its calculated pattern of behavior. Only the lowest two allyl ligand orbitals ($b_1(1)$ and a_2) interact significantly with palladium.[25] Thus, whereas the shift of the outer carbon atoms should vary markedly with the extent of delocalization of a_2, the nonbonding π orbital (an upfield shift of *ca.* 48 ppm/electron added), the central carbon atom shift is expected to vary little (less than 3 ppm) with such changes in both the bonding ($b_1(1)$) and nonbonding π orbitals; it should therefore be relatively independent of its environment. However, experimental results show that shifts of both types of atoms vary significantly from complex to complex,[24,26] even when only one metal is considered. More accurate molecular orbital calculations could be employed, but these would surely not affect the conclusion that the effects considered by this model are quantitatively unimportant. Any successful treatment of π-bonded carbon chemical shifts must take the effects of the transition metal more directly and completely into account.

It is noteworthy that two of the first workers[27] to measure ^{13}C chemical shifts in transition metal complexes concluded in 1965 that "No convincing explanation of these results within the framework of the current approximate shielding theory has been found." Such pessimism unfortunately is still warranted a decade later.

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Rhenium(I) Complexes of (*o*-Cyanophenyl)diphenylphosphine

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Sir:

Dinitriles and phosphinenitriles have recently been investigated as bidentate ligands potentially capable of coordinating through the nitrile group(s) π electrons. From spectroscopic and analytical data it has been proposed that (*o*-cyanophenyl)diphenylphosphine (L) forms dimeric π complexes with rhenium(I)[1] (**1**) and that both succinonitrile and L form monomeric π complexes with manganese(I)[1-3] (**2** and **3**). The ligand

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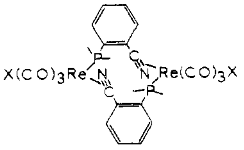
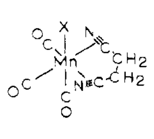
Table I. Analytical Data for $[Re(CO)_3LX]_2$

	Analyses, %									
	C		H		N		P		X	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$[Re(CO)_3LCl]_2$	44.56	44.73	2.38	2.52	2.36	2.27	5.22		5.98	5.83
$[Re(CO)_3LBr]_2$	41.45	41.29	2.21	2.27	2.20	2.18	4.86	4.64	12.54	12.64

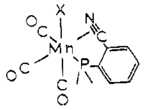
properties of (2-cyanoethyl)diphenylphosphine (L′), which is analogous to (*o*-cyanophenyl)diphenylphosphine, have also been investigated utilizing rhenium(I).[4] In contrast to L in 1, it was proposed that L′ functions as a bridging ligand with the nitrile group σ bonding to rhenium(I) through the nitrile nitrogen electron pair as shown in 4.[4]



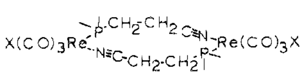
1



2



3



4

The majority of metal–nitrile complexes involve σ bonding through the nitrile nitrogens.[5,6] π coordination, however, has been proposed for several complexes[1,2,3,7-9] but confirmed for only two molecules $Pt[(C_6H_5)_3P]_2(CF_3CN)$[10] and $[Ni(CO)\cdot(C_5H_5NCN)]_2$.[11] The succinonitrile complexes, 2, are examples of proposed π complexes.[2] The claim of π bonding in these is controversial and evidence has been presented that suggests the complexes may be either halogen-bridged dimers with the succinonitrile ligands functioning as monodentate σ donors[12] or mixtures of monomeric and dimeric complexes.[13]

For the majority of metal–nitrile complexes, infrared spectroscopic studies have been utilized to determine the mode of nitrile coordination. It is generally accepted that σ bonding is accompanied by an increase in ν(CN) over that observed for the free ligand.[5,14] In contrast π coordination is expected to shift the ν(CN) bands to lower frequencies as observed for $Pt[C_6H_5)_3P]_2(CF_3CN)$.[10]

From the spectroscopic standpoint, there is one feature common to all the aforementioned complexes, 1–4. All display very weak or undetectable ν(CN) bands in their infrared spectra in the region expected for σ-bonded nitrile groups. The absence of detectable or presence of very weak ν(CN) bands in nitrile complexes is not without precedence and has been noted for $Re[(C_6H_5)_3P]_2(CH_3CN)Cl_3$[15] which is known to contain a linear Re–N–C– grouping.[16] This intensity pattern of infrared bands has also been noted for a series of cationic methylplatinum(II)–nitrile complexes, but for these, studies proved the ν(CN) to be sharp and intense in the Raman spectra.[8] Raman spectral data for two halotricarbonylrhenium(I)–nitrile complexes, $[Re(CO)_3L'X]_2$,[4] 4, and $[Re(CO)_3(CNCH_2CH_2CN)X]_2$[12] have also been reported, and both display intense ν(CN) bands assigned to σ-bonded nitrile groups. Thus Raman data have proved to be a valuable supplement to ir data in the detection and study of coordinated nitrile groups.

During the course of our studies on transition metal–nitrile complexes we synthesized halotricarbonylrhenium complexes of (*o*-cyanophenyl)diphenylphosphine (L) which were assigned the stoichiometry $[Re(CO)_3LX]_n$ on the basis of elemental analyses. While our studies were in progress, molecules of identical stoichiometry, namely, 1, were described.[1] We wish to communicate some additional results including an improved synthesis which yields unsolvated complexes, far-infrared data for the bromo complex, and Raman data. Of particular interest are the Raman data which suggest that the nitrile portion of L is σ, rather than π, bonded to the rhenium.

In a typical synthesis, equimolar amounts (1.23 mmol) of (*o*-cyanophenyl)diphenylphosphine and halopentacarbonylrhenium(I) (chloro or bromo) were refluxed in 60 ml of benzene for 4 hr under argon. During the initial stages of the reaction the reactants dissolved, but the products precipitated as colorless solids. After the reaction period the products were collected on a filter and washed with 10 ml of hot benzene followed by 10 ml of hot dichloromethane. The yields were 83 and 79% respectively for the bromo and chloro derivatives. Analytical data for the previously unreported chloro complex as well as the bromo complex are recorded in Table I.

We have also synthesized the bromo complex in dichloromethane as described by Payne[1] so that an accurate spectroscopic comparison could be made with the complexes synthesized in benzene as described above. The complexes from both preparative methods yield ir spectra in the KBr region (when recorded in Nujol or KBr) that are identical. Furthermore, the data in the ν(CO) region are in excellent agreement with those reported by Payne.[1] Thus, when the spectra are recorded in chloroform, three strong ν(CO) bands are observed at 2040, 1955, and 1920 cm^{-1}. Regardless of the preparative method, however, very weak bands are observed in the ν(CN) region at 2250 cm^{-1}; these are very intense in the Raman spectra. From these data we conclude that, within the limits of infrared and Raman measurements, the complexes synthesized in dichloromethane are identical with those from benzene and are most likely identical with

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Table II. Infrared and Raman Data for $[Re(CO)_3LX]_2$

	ν(CN)		ν(MX)
	Raman[a]	Ir[b]	Ir[c]
$[Re(CO)_3LCl]_2$	2250	2246 vw	270
$[Re(CO)_3LBr]_2$	2250	2250 vw	185

[a] Solid sample. [b] Nujol mull on NaCl plates (Beckman IR-10). [c] Nujol mull on polyethylene plates (Beckman IR-11).

those reported by Payne.[1] Furthermore, the position of the nitrile bands at frequencies 25 cm^{-1} higher than observed for the free nitrile strongly suggests that L, like L′ in **4**, functions as a bridging ligand using the phosphorus and nitrogen lone pairs.

Even though the rhenium samples showed no visible evidence of decomposition in the laser beam, ir spectra were obtained on all spectroscopic samples before and after Raman analysis. In all cases they remained unchanged, which further substantiates the validity of these data.

In agreement with the data reported by Payne,[1] we observed six bands in the terminal carbonyl absorption region of the infrared spectra of the complexes when recorded in Nujol. Payne, however, assigned the band at 1920 cm^{-1}, observed for both the bromo and chloro complexes, to the ν(CN) vibration. This very intense sixth band can readily be accounted for if a σ-bonded formulation is assumed. As many as six fundamental bands could result from a $Re_2(CO)_6L_2X_2$ molecule or six bands are possible from the solid-state splitting of fewer than six fundamentals.

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Registry No. $[Re(CO)_3LCl]_2$, 52540-43-9; $[Re(CO)_3LBr]_2$, 52540-44-0.

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