systems as observed for the carbonyl-stretching frequencies (A mode) in the infrared spectrum and indirectly support the interpretation suggested by Lundquist and Cais that these bands are associated with metal–carbon monoxide transitions.

The similarities in the A bands and the carbonyl-stretching frequencies (A mode) of the borazine and benzene complexes indicate that the chromium–carbon monoxide bonding in these complexes is very similar. In addition, because of the similarity of the C band absorptions for acetonitrile, ammonia, and borazine complexes, it is suggested that this band correlates with the π-acceptor character as well as the donor character of the noncarbonyl ligands (arene, borazine, etc.) involved in these metal–ligand electronic transitions. This conclusion is supported by the bathochromic shifts of the C bands which occur because of conjugation by unsaturated substituents on the arene or cyclopentadienyl ligands reported by Lundquist and Cais.[28]

This interpretation suggests that the borazine ring is a significantly poorer π-acceptor ligand than is an arene moiety, although both ligands have similar donor characteristics; this is consistent with the presence of a puckered borazine ring in the complexes containing this ligand.

π-Coordinated Nitrile Derivatives of Halopentacarbonylmanganese(I) and -rhenium(I)

DAVID H. PAYNE,[*1] ZIE A. PAYNE, RAYMOND ROHMER, and HERSCHEL FRYE

The application of *o*-cyanophenyldiphenylphosphine to the synthesis of the first π-coordinated, mononitrile–phosphine complexes of halopentacarbonyl group VII metals is described. The molecular formula of these complexes $\{[M(CO)_3LX]_y$ where $L = o\text{-}NC(C_6H_4)P(C_6H_5)_2$; $M = Mn$, $X = Cl$, Br, or I, $y = 1$; $M = Re$, $X = Cl$ or Br, $y = 2\}$ and their infrared spectra are consistent with coordination of both the phosphorus atom and the C≡N bond to the group VII metal. The lowering of the C≡N stretching frequency upon π coordination of the nitrile groups to group VII metals is determined from infrared spectral measurements and is used to assess the degree of interaction between nitrile and metal in these complexes. The carbonyl-stretching frequencies are used to compare the ligand's ability to compete for metal π-electron density.

Introduction

It has been shown that isocyanate,[2] amine–nitrile,[3-7] and dinitrile[8,9] ligands are capable of coordination through the triple bond of their nitrile groups. We now report the extension of this series by the π-coordination of a phosphine–nitrile ligand with halopentacarbonylmanganese(I) and -rhenium(I). The phosphine–nitrile used in these preparations is the ligand, *o*-cyanophenyldiphenylphosphine[10] (structure I)

I
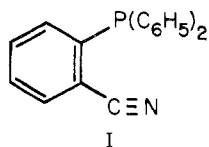
In a preliminary report of some of this material,[11] the

assignment of π coordination in the manganese(I) derivatives (structure II) was in part based upon the analogous π-nitrile complexes of succinonitrile (structure III).[8,9] Although evi-

II

III
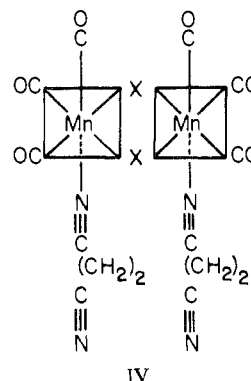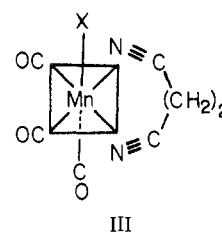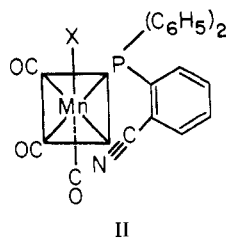
IV

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dence has been presented[12] which would reformulate structure III as the σ-coordinated, dimeric complex (structure IV), later studies[13] indicate that both the kinetically favored π complexes (structure III) and the thermodynamically favored σ complexes (structure IV) exist. This independent synthesis of the *o*-cyanophenyldiphenylphosphine derivatives not only lends more evidence to the existence of π-nitrile coordinated complexes but provides the first examples of mononitrile–phosphine complexes where the aromatic ring provides the bridge in the chelate ring.

Experimental Section

Starting Materials. *o*-NC(C$_6$H$_4$)P(C$_6$H$_5$)$_2$,[10] Mn(CO)$_5$Cl,[14] Mn(CO)$_5$Br,[14] and Mn(CO)$_5$I[15] were prepared as previously described. Re(CO)$_5$Cl and Re(CO)$_5$Br were obtained from Pressure Chemical Co. All reactions were performed under an atmosphere of prepurified, dried argon.

Measurements. Infrared spectra were recorded in the region 4000–250 cm^{-1} on a Perkin-Elmer Model 457 spectrophotometer. The spectra were obtained in the solid state as Nujol mulls between KBr plates or as cesium iodide pellets. All of the spectra were carefully calibrated with polystyrene film. Microanalysis and molecular weight measurements were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., and/or by Chemalytics Inc., Tempe, Ariz.

Preparation of Compounds. Mn(CO)$_3$[*o*-NC(C$_6$H$_4$)P(C$_6$H$_5$)$_2$]X. A detailed preparation of Mn(CO)$_3$[*o*-NC(C$_6$H$_4$)P(C$_6$H$_5$)$_2$]I is given below. The chloride and bromide derivatives may be prepared similarly.[11]

Mn(CO)$_5$I (0.322 g, 1.0 mmol) and *o*-NC(C$_6$H$_4$)P(C$_6$H$_5$)$_2$ (0.288 g, 1.0 mmol) were refluxed (20 hr) in CH$_2$Cl$_2$ (50 ml). The mixture was cooled and the crystals were collected by filtration, washed with CH$_2$Cl$_2$, and dried under vacuum (10^{-3} mm) to give 0.331 g (60.0%) of orange crystals which decomposed at 149°.

Preparation of Re$_2$(CO)$_6$[*o*-NC(C$_6$H$_4$)P(C$_6$H$_5$)$_2$]$_2$Cl$_2$·CH$_2$Cl$_2$. Re(CO)$_5$Cl (0.362 g, 1.0 mmol) and *o*-NC(C$_6$H$_4$)P(C$_6$H$_5$)$_2$ (0.288 g, 1.0 mmol) were refluxed (24 hr) in CH$_2$Cl$_2$ (50 ml). The mixture was cooled and the crystals were collected by filtration, washed with CH$_2$Cl$_2$, and dried under vacuum (10^{-3} mm) to give 0.226 g (35.6%) of white crystals which decomposed at 218°. *Anal.* Calcd for Re$_2$(CO)$_6$[*o*-NC(C$_6$H$_4$)P(C$_6$H$_5$)$_2$]$_2$Cl$_2$·CH$_2$Cl$_2$: C, 42.50; H, 2.39; N, 2.20; P, 4.87; Cl, 11.18; O, 7.56; Re, 29.31. Found: C, 42.47; H, 2.35; N, 2.24; P. 5.29; Cl, 11.21; O, 7.82; Re, 29.02.

**Preparation of Re$_2$(CO)$_6$[*o*-NC(C$_6$H$_4$)P(C$_6$H$_5$)$_2$]$_2$Br$_2$.** Re(CO)$_5$-Br (0.406 g, 1.0 mmol) and *o*-NC(C$_6$H$_4$)P(C$_6$H$_5$)$_2$ (0.288 g, 1.0 mmol) were refluxed (4 days) in CH$_2$Cl$_2$ (50 ml). The mixture was cooled and the crystals were collected by filtration, washed with CH$_2$Cl$_2$, and dried under vacuum (10^{-3} mm) to give 0.118 g (18.5%) of white crystals which decomposed at 220°. *Anal.* Calcd for Re$_2$(CO)$_6$[*o*-NC(C$_6$H$_4$)P(C$_6$H$_5$)$_2$]$_2$Br$_2$: C, 41.43; H, 2.22; N, 2.20; P. 4.86; O, 7.53; mol wt, 1274. Found: C, 41.07; H, 2.15; N, 1.93; P, 4.40; O, 8.10; mol wt, 1230 by osmometry in pyridine.

Results

o-Cyanophenyldiphenylphosphine derivatives of group VII metal pentacarbonyl halides were prepared by direct reaction in dichloromethane solution at reflux temperature. As evidenced by elemental and molecular weight analysis, two molecules of carbon monoxide were replaced on each metal atom by a coordinating group of the ligand to give compounds of general formula [M(CO)$_3$LX]$_y$ (where L = *o*-NC(C$_6$H$_4$)P(C$_6$H$_5$)$_2$; M = Mn,[11] X = Cl, Br, or I, *y* = 1; M = Re, X = Cl or Br, *y* = 2). The chloride derivatives in each case contain one molecule of dichloromethane as solvent of crystallization. Although the compounds are either insoluble or reactive with most solvents, molecular weight measurements were obtained on the bromide derivatives by vapor pressure osmometry. The results indicate that the manganese

derivative is monomeric[11] and the rhenium is dimeric. The manganese compounds range from yellow to orange whereas the rhenium compounds are white. Being extremely sensitive to light, the compounds were stored in the dark under argon. The rhenium complexes are more stable than those of manganese and are slightly soluble in chloroform.

The ligand may wholly or partially be displaced by amine, nitrile, phosphine, or ligands with active hydrogens. However, the long reaction time attests to the validity of the molecular weight analysis mentioned above. Acetonitrile has previously been reported to react with π-nitrile complexes.[9] Our studies indicate that acetonitrile replaces the π-nitrile group but not the phosphorus atom. Preliminary investigation of the reaction product of *o*-cyanophenyldiphenylphosphine complexes and acetonitrile has revealed the characteristics of the compound shown in structure V.

V
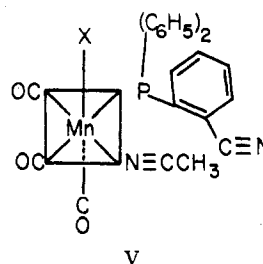
Additional evidence for the coordination of *o*-cyanophenyldiphenylphosphine is provided by the infrared data, which are summarized in Table I. The 2225-cm^{-1} band assigned to the nitrile-stretching frequency of the free ligand is clearly absent from the spectra of the complexes. The ligand may react with metals in a number of ways. As a monodentate ligand, it could react either through the phosphorus atom or the nitrile group. The preparation of the phosphorus-coordinated platinum derivative Pt[*o*-NC(C$_6$H$_4$)P(C$_6$H$_5$)$_2$]$_2$Cl$_2$[10] indicates that phosphorus is the better coordinating species. In this case, the frequency of the uncoordinated nitrile group increased +5 cm^{-1} to 2230 cm^{-1}. As a bidentate ligand in the trimeric platinum complex {Pt[*o*-NC(C$_6$H$_4$)P(C$_6$H$_5$)$_2$]-Cl$_2$}$_3$,[10] the nitrile increased its stretching frequency by +57 cm^{-1} to 2282 cm^{-1} when coordinated through its lone pair of electrons. It has also been shown that nitrogen coordination can occur in conjunction with a nitrile isomerization to an imino ether as in the palladium derivative Pd[*o*-HN=C-(OC$_2$H$_5$)(C$_6$H$_4$)P(C$_6$H$_5$)$_2$]Cl$_2$.[16] The nitrogen-coordinated imino ether decreased its stretching frequency to 1633 cm^{-1} which is characteristic of the double bond of an imine. Other nitrile complexes have been coordinated by simultaneous carbon and nitrogen bonding[17] or by π coordination of the imine derivative.[18] The lack of new bands in the C=N or N–H regions of the infrared spectra makes these possibilities very unlikely.

In the 2400–1800-cm^{-1} region of the infrared, the manganese complexes have four bands and are analogous to the dinitrile derivatives previously reported.[9] A new band occurs near 1973 cm^{-1} for these complexes and is characteristic of a nitrile group coordinated through the π electrons of its triple bond.[2–9] This assignment has been confirmed by an X-ray determination in one case.[4] The major change is an additional decrease in frequency of the π-coordinated nitrile.

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Table I. Infrared Spectra of the Nitriles and Their Complexes[a]

Compound	ν(CN), cm^{-1}	ν(CO), cm^{-1}	ν(MX),[c,g] cm^{-1}
o-NC(C$_6$H$_4$)P(C$_6$H$_5$)$_2$[g]	2225 m		
NCCH$_2$CN[e]	2278 m		
o-NC(C$_6$H$_4$)CN[e,i]	2237 m		
NCCH$_2$CH$_2$CH$_2$CN[e,i]	2257 m		
NCCH$_2$CH$_2$CN[e,i]	2257 m		
NCCH$_2$CH$_2$P(C$_6$H$_5$)$_2$[g,k]	2230 m, 2250		
Mn(CO)$_3$[o-NC(C$_6$H$_4$)P(C$_6$H$_5$)$_2$]Cl·CH$_2$Cl$_2$	1973 ms	2042 s, 1958 s, 1937 s	260 m
Mn(CO)$_3$(NCCH$_2$CN)Cl[i]	2066 sh	2045 s, 1969 s, 1938 s	287 m[j]
Mn(CO)$_3$(NCCH$_2$CH$_2$CN)Cl[i]	2070 s	2024 s, 1982 s, 1923 s	280 m
Mn(CO)$_3$[o-NC(C$_6$H$_4$)P(C$_6$H$_5$)$_2$]Br	1974 s	2044 s, 1959 s, 1938 s	
Mn(CO)$_3$(NCCH$_2$CN)Br[i]	2062 sh	2049 s, 1957 s, 1936 s	228[j]
Mn(CO)$_3$[o-NC(C$_6$H$_4$)CN] Br[i]	2041 sh	2024 s, 1951 s, 1923 s	
Mn(CO)$_3$(NCCH$_2$CH$_2$CN)Br[i]	2062 m	2041 s, 1957 s, 1931 s	
Mn(CO)$_3$(NCCH$_2$CH$_2$CN)Br[i]	2072 m	2045 s, 1957 s, 1938 s	220[j]
Mn(CO)$_3$[o-NC(C$_6$H$_4$)P(C$_6$H$_5$)$_2$]I	1973 ms	2041 s, 1957 s, 1938 s	
Mn(CO)$_3$(NCCH$_2$CH$_2$CN)I[f,h]	2074 ms	2002 s, 1978 s, 1935 s	
Re$_2$(CO)$_6$[o-NC(C$_6$H$_4$)P(C$_6$H$_5$)$_2$]$_2$Cl$_2$·CH$_2$Cl$_2$	1920 m, sh	2038 s, 1974 ms, 1959 s 1930 m, 1906 s	277 mw
Re$_2$(CO)$_6$[o-NC(C$_6$H$_4$)P(C$_6$H$_5$)$_2$]$_2$Cl$_2$·CH$_2$Cl$_2$[e]	b	2044 s, 1955 s, 1914 s	
Re(CO)$_3$(NCCH$_2$CN)Cl[i]	2045 sh	2030 s, 1930 s, 1910 s	288 m[j]
Re(CO)$_3$(NCCH$_2$CH$_2$CH$_2$CN)Cl[i]	d	2037 s, 1942 s, 1905 s	288 m[j]
Re(CO)$_3$(NCCH$_2$CH$_2$CN)Cl[i]	2041 sh	2033 s, 1931 s, 1905 s	275 ms
Re$_2$(CO)$_6$[NCCH$_2$CH$_2$P(C$_6$H$_5$)$_2$]$_2$Cl$_2$[e,k]	2295 w	2040 s, 1980 s, 1940 s	288 s
Re$_2$(CO)$_6$[o-NC(C$_6$H$_4$)P(C$_6$H$_5$)$_2$]$_2$Br$_2$	1920 ms	2040 s, 1974 m, 1962 s 1932 m, 1908 s	
Re$_2$(CO)$_6$[o-NC(C$_6$H$_4$)P(C$_6$H$_5$)$_2$]$_2$Br$_2$[e]	b	2042 s, 1956 s, 1919 s	
Re(CO)$_3$(NCCH$_2$CN)Br[i]	2045 sh	2030 s, 1934 s, 1910 s	205[j]
Re(CO)$_3$(NCCH$_2$CH$_2$CH$_2$CN)Br[i]	2045 sh	2028 s, 1923 s, 1905 s	
Re(CO)$_3$(NCCH$_2$CH$_2$CN)Br[i]	2045 sh	2031 s, 1927 s, 1901 s	195[j]
Re$_2$(CO)$_6$[NCCH$_2$CH$_2$P(C$_6$H$_5$)$_2$]$_2$Br$_2$[e,k]	2295 w	2040 s, 1980 s, 1940 s	198 s

[a] All bands, except where indicated, were recorded as Nujol mulls between KBr disks. Abbreviations: vs, very strong; s, strong; ms, medium strong; m, medium; mw, medium weak; w, weak; vw, very weak; b, broad; sh, shoulder. [b] Probably covered by the lowest frequency carbonyl band. [c] M = Mn, Re; X = Cl, Br, I. [d] Probably covered by the highest frequency carbonyl band. [e] Chloroform solution. [f] Acetone solution. [g] KBr or CsI pellet. [h] Reference 8. [i] Reference 9. [j] Reference 13. [k] Reference 19.

The carbonyl-stretching frequencies were easily assigned because they remain in the same region as the dinitrile derivatives. The ν(MX) are also included in Table I. In accord with the dinitrile complexes, one Mn–Cl band is in agreement with the monomeric nature of these chelates.

The rhenium derivatives present an unusual variation. Nujol spectra consist of six, sharp, medium to strong bands in the 2400–1800-cm^{-1} region. We have assigned the 1920-cm^{-1} band to the stretching frequency of the π-coordinated nitrile group on the basis of its expected decrease in frequency with rhenium and its sharper and weaker appearance in contrast to the carbonyl bands. Also, since only three bands appear in chloroform solution, the nitrile band must be in close proximity to one of them. The 1920-cm^{-1} band best fits all of these conditions. We expect that the nitrile band is hidden by the lowest frequency carbonyl band in the chloroform spectra. Five bands in Nujol and three in chloroform are characteristic of the carbonyl stretching of dimeric complexes with general formula M$_2$(CO)$_6$L$_4$ (where M = Mn, Re; L is a halide or nitrile ligand[19,20]). The molecular weight measurement and infrared data support a dimeric structure. The observation of only one Re–Cl band indicates a terminal halogen.[19] The complexes are characterized as shown in structure VI. Like the halopentacarbonylrhenium-(I) derivatives of o-cyanoethyldiphenylphosphine,[19] o-cyanophenyldiphenylphosphine has been previously observed as a bridging ligand.[10] Accordingly, the symmetrical structure with one phosphorus on each metal atom has been assigned. The infrared spectra of the analogous o-cyanoethyldiphenylphosphine derivatives have been included in Table I for

VI
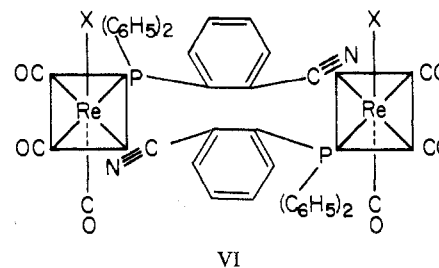
comparison. The only difference is that these aliphatic complexes have the thermodynamically favored, σ-nitrile coordination.

Discussion

Some comparisons of carbonyl- and nitrile-stretching frequencies are given in Table II. The decrease in ν(CN) from that of the uncoordinated nitrile consistently decreases in the order o-NC(C$_6$H$_4$)P(C$_6$H$_5$)$_2$ > NCCH$_2$CN > o-NC(C$_6$H$_4$)CN $\geqslant$ NC(CH$_2$)$_3$CN $\geqslant$ NC(CH$_2$)CN. The complexes of o-cyanophenyldiphenylphosphine provide the largest decrease of ν(CN) so far observed. The large $\Delta\nu$(CN) is not unexpected as π-coordinated acetylenic complexes have been reported with $\Delta\nu$(C$\equiv$C) as large as -250 cm^{-1}.[21] Nonlinear molecular nitrogen complexes have been observed with $\Delta\nu$(N$\equiv$N) as great as -330 cm^{-1}.[22] The large dependence of $\Delta\nu$(CN) on the specific ligand used indicates that ν(CN) is not a good measure of bond strength; however, the large decrease in $\Delta\nu$(CN) is expected to reflect an increase in the π metal-nitrile interaction. This relationship is commonly acknow-

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Table II. $\Delta\nu(CN)$, $d[\Delta\nu(CN)]$, $\Sigma(CO)$, and $\Delta\Sigma(CO)$ for Bromotricarbonyls of Mn and Re

Compound	$\Delta\nu(CN),^a$ cm^{-1}	$d[\Delta\nu(CN)],^b$ cm^{-1}	$\Sigma(CO),^c$ cm^{-1}	$\Delta\Sigma(CO),^d$ cm^{-1}
Mn(CO)$_3$Br[o-NC(C$_6$H$_4$)P(C$_6$H$_5$)$_2$]^h	-251	0	5941	0
Mn(CO)$_3$Br[NCCH$_2$CN]^{e,h}	-216	-35	5942	-1
Mn(CO)$_3$Br[o-NC(C$_6$H$_4$)CN]^{e,h}	-196	-55	5898	$+43$
Mn(CO)$_3$Br[NCCH$_2$CH$_2$CH$_2$CN]^{e,h}	-195	-56	5929	$+12$
Mn(CO)$_3$Br[NCCH$_2$CH$_2$CN]^{e,h}	-185	-66	5940	$+1$
Mn(CO)$_3$Br[P(OC$_6$H$_5$)$_3$]$_2^{g,i}$			6002	-61
Mn(CO)$_3$Br[o-H$_2$C=CH(C$_6$H$_4$)P(C$_6$H$_5$)$_2$]^{f,j}			5981	-40
Mn(CO)$_3$Br[P(C$_6$H$_5$)$_3$]$_2^{g,i}$			5917	$+24$
Mn(CO)$_3$Br[NH$_2$(C$_6$H$_5$)]$_2^{g,i}$			5880	$+61$
Re$_2$(CO)$_6$Br$_2$[o-NC(C$_6$H$_4$)P(C$_6$H$_5$)$_2$]$_2^i$	-305	0	5917	0
Re(CO)$_3$Br[NCCH$_2$CN]^{e,h}	-233	-72	5874	$+43$
Re(CO)$_3$Br[NCCH$_2$CH$_2$CH$_2$CN]^{e,h}	-212	-93	5856	$+61$
Re(CO)$_3$Br[NCCH$_2$CH$_2$CN]^{e,h}	-212	-93	5859	$+58$

^{a} $\Delta\nu(CN) = \nu(CN)_{complex} - \nu(CN)_{ligand}$. ^{b} $d[\Delta\nu(CN)] = \Delta\nu(CN)_{o\text{-cyanophenyldiphenylphosphine complex}} - \Delta\nu(CN)_{complex}$. ^{c} $\Sigma(CO) = (CO)_1 + \cdots + (CO)_n$. ^{d} $\Delta\Sigma(CO) = \Sigma(CO)_{o\text{-cyanophenyldiphenylphosphine complex}} - \Sigma(CO)_{complex}$. ^{e} Reference 9. ^{f} Reference 25. ^{g} D. M. Adams, "Metal–Ligand and Related Vibrations," St. Martins Press, New York, N. Y., 1968, p 147. ^{h} Nujol. ^{i} Chloroform. ^{j} Carbon tetrachloride.

ledged for π-coordinated olefinic[23] and acetylenic[24] compounds. Indeed, the greater availability of π-bonding orbitals on rhenium would be expected to form stronger bonds than manganese. Accordingly, we have observed that $\Delta\nu(CN)$ is significantly larger for all of the rhenium derivatives. The metal–nitrile bond strength appears to vary with the metal in this homologous series in the order Re > Mn. The decrease of $\Delta\nu(CN)$ parallels the decrease of $\Delta\nu(C\equiv C)$ when rhenium is substituted for manganese.[25] The order also fits in with the somewhat greater stability observed for the rhenium complexes as compared to the manganese derivatives. The increase of $\Delta\nu(CN)$ for Re over Mn follows the increase of metal d electrons and a relative decrease of available metal charge on Re. These factors indicate that π metal to nitrile back-bonding is more important than bonding π nitrile to metal bonding. The large value of $\Delta\nu(CN)$ for o-cyanophenyldiphenylphosphine may be understood in terms of its ability to increase this back-donation by recirculating electron density through the conjugated structure. The phosphorus atom is apparently more efficient in this transfer than the nitrile group since phthalonitrile has a $\Delta\nu(CN)$ some -55 cm^{-1} lower than π-coordinated o-cyanophenyldiphenylphosphine.

Carbonyl frequencies have been used as an indication of a ligand's ability to compete for metal π-electron density.[26,27] For the rhenium derivatives, our results indicate that the increase of $\Delta\nu(CN)$ for π-nitrile complexes closely parallels the ligand's ability to compete for metal π-electron density.

This is expected due to the more important role of metal to ligand back-bonding with the greater availability of π electrons on rhenium. There is no ordered relationship between $\Delta\nu(CN)$ and $\Sigma(CO)$ for the manganese compounds. The changes in order and magnitude are attributed to the larger role of a new, as yet uncharacterized interaction between the ligand and the π-electron deficient manganese(I) ion. The order of decreasing ability to compete for the metal π electrons of bromotricarbonylmanganese(I) is [P(OC$_6$H$_5$)$_3$]$_2 > o$-H$_2$C= CH(C$_6$H$_4$)P(C$_6$H$_5$)$_2 >$ NCCH$_2$CN $\geqslant o$-NC(C$_6$H$_4$)P(C$_6$H$_5$)$_2 \geqslant$ NC(CH$_2$)$_2$CN $>$ NC(CH$_2$)$_3$CN $>$ [P(C$_6$H$_5$)$_3$]$_2 > o$-NC(C$_6$H$_4$)- CN $>$ [NH$_2$(C$_6$H$_5$)]$_2$. The olefinic bond of o-styrylphenyldiphenylphosphine is a better competitor than the nitrile group. All of the nitriles are better competitors than triphenylphosphine except phthalonitrile which is close to aniline in its inability to accept back-donation from the metal. For phthalonitrile, the low $\Sigma(CO)$ and large $\Delta\nu(CN)$ indicate that the secondary effect is of comparable importance to back-bonding. In order to better characterize the secondary effect, we are currently investigating the nitrile shift of the complexes as a function of oxidation state.

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