Table II. Rate Constants and Activation Parameters

reaction	k_2(24 °C), M^{-1} s^{-1}	ΔH^*, kJ mol^{-1}	ΔS^*, J K^{-1} mol^{-1}
$Ni(CN)_4^{2-}$ + CN^- →	>5 × 10^5		
$Pd(CN)_4^{2-}$ + CN^- →	120	17 ± 2	−178 ± 7
$Pt(CN)_4^{2-}$ + CN^- →	26	26 ± 3	−143 ± 8
$Au(CN)_4^-$ + CN^- →	3900	28 ± 1	−100 ± 3
trans-[$Ni(PEt_3)_2$(*o*-tol)Cl] + EtOH →	330[a]		
trans-[$Pd(PEt_3)_2$(*o*-tol)Cl] + EtOH →	0.58[a]		
trans-[$Pt(PEt_3)_2$(*o*-tol)Cl] + EtOH →	6.7 × 10^{-6} [a]		
[Pt(dien)Cl]$^+$ + Br^- →	5.3 × 10^{-3} [b,d]	59[b]	−96[b]
[Au(dien)Cl]$^{2+}$ + Br^- →	154[b,c]	54[b]	−17[b]

[a] Reference 11. Values are for solvent reaction in ethanol; k_1 in units of s^{-1}; overall reaction involved pyridine replacement of Cl^-; 25 °C. [b] Reference 12. [c] 20 °C. [d] 25 °C.

complex, and the second-order rate constants, k_2, were determined from the slopes. Activation parameters ΔH^* and ΔS^* were calculated from data taken at four different temperatures from 30 to 60 °C. In the case of $Ni(CN)_4^{2-}$, no line broadening could be detected within experimental error. Therefore, only a lower limit can be placed on the rate of CN^- exchange. On the assumption that the broadening was <1 Hz, k_2 is estimated to be >5 × 10^5 s^{-1} M^{-1} (in the fast-exchange region[9]).

Results and Discussion

The CN^--exchange rate data for $Pd(CN)_4^{2-}$, $Pt(CN)_4^{2-}$, and $Au(CN)_4^-$ obtained from ^{13}C NMR are collected in Table I and are consistent with the simple rate law in eq 1. The rate

$$\text{rate} = k_2[M(CN)_4^{n-}][CN^-] \quad (1)$$

laws for most square-planar substitution reactions have two terms:[10] a term that depends on the substituting reagent analogous to eq 1 and a second term independent of reagent concentration, which in the present case should have the form $k_1[M(CN)_4^{n-}]$. The reagent-dependent term is visualized as resulting from an associative replacement involving a five-coordinate transition state. The reagent-independent term corresponds to a rate-limiting solvent substitution (presumably involving an associative five-coordinate transition state also) followed by a fast solvent replacement by the reagent. Both terms would lead to the same substituted product, in the present case to CN^- exchange. However, careful examination of the data was made for such a CN^--independent term, but plots of k_{obsd} vs. [CN^-] gave good straight lines that passed through the origin within experimental error. If a CN^--independent path for the exchange exists, its contribution to the overall rate is very small and $k_2[CN^-] \gg k_1$. Rate constants and activation parameters are summarized in Table II along with some data for some related reactions for comparison. The slowest rates measured in our experiments correspond to $t_{1/2}$ ~ 0.5–2 s so that the lack of quantitative data from the earlier radioisotope studies[4–6] can be easily understood.

The CN^--exchange rates are in the order Ni(II) ≫ Au(III) > Pd(II) > Pt(II) (relative k_2 at 24 °C >2 × 10^4:150:4.6:1), with $Pt(CN)_4^{2-}$ being the most inert. Though data are limited, a similar reactivity order has been observed for other square-planar substitution reactions as the metal ion is changed. For example, in the Cl^- replacement by pyridine in *trans*-[$M(PEt_3)_2$(*o*-tol)Cl], the relative rates of the rate-limiting ethanol substitution (reagent-independent path) at 25 °C (Table II) for Ni(II), Pd(II), and Pt(II) are 5 × 10^6:10^5:1, respectively;[11] for Cl^- replacement by Br^- in [M(dien)Cl]$^{n+}$ the relative rates for Au(III) and Pt(II) are ~3 × 10^4:1.[12] It is interesting that the CN^--exchange rate variation between $Pd(CN)_4^{2-}$ and $Pt(CN)_4^{2-}$, and to a lesser extent between $Au(CN)_4^-$ and $Pt(CN)_4^{2-}$, is smaller than for the other reactions among square-planar complexes as the metal ion is changed. From the trend in activation parameters, changes in ΔH^* and ΔS^* are partly compensating for the CN^- exchange. Thus, ΔH^* for CN^- exchange with $Pd(CN)_4^{2-}$ is ~9 kJ mol^{-1} more favorable than for $Pt(CN)_4^{2-}$, but ΔS^* is 35 J K^{-1} mol^{-1} more unfavorable. Similarly the much higher rate for $Au(CN)_4^-$ can be traced to a more favorable (less negative) ΔS^* since the ΔH^* is larger than for either $Pd(CN)_4^{2-}$ or $Pt(CN)_4^{2-}$. A similar trend in ΔS^* is observed for [M(dien)Cl]$^{n+}$ + Br^- (Table II). The exceptionally high reactivity of $Ni(CN)_4^{2-}$ to CN^- exchange is undoubtedly due to the stability of five-coordinate $Ni(CN)_5^{3-}$, which may be similar to reaction intermediates or the associative transition state. Salts of $Ni(CN)_5^{3-}$ have been isolated,[13] but there is no evidence that five-coordinate CN^- complexes of Pd(II), Pt(II), or Au(III) exist either in solution or in the solid state.

Registry No. CN^-, 57-12-5; $Ni(CN)_4^{2-}$, 48042-08-6; $Pd(CN)_4^{2-}$, 15004-87-2; $Pt(CN)_4^{2-}$, 15004-88-3; $Au(CN)_4^{2-}$, 14263-59-3.

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A Molybdenum-95 NMR Study of Some *cis*-$Mo(CO)_4(PPh_2XR)_2$ and $Mo(CO)_4(PPh_2YPPh_2)$ Complexes. Correlation between Molybdenum-95 NMR Chemical Shifts and UV–Vis Absorption Band Wavelengths

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Recent ^{95}Mo NMR studies of molybdenum(VI) complexes[1–4] and molybdenum(0) carbonyl complexes containing π-arene,[5,6] Schiff base,[7,8] and organophosphine[9–11] ligands have shown the ^{95}Mo chemical shift to be extremely sensitive to the ligand environment (of the molybdenum) and have suggested that this technique may serve as a probe for subtle steric and electronic effects in molybdenum-containing catalysts and enzymes. First, however, a better understanding of the manner in which the steric and electronic properties of the ligands influence the ^{95}Mo chemical shift is desirable. In two previous studies we have shown that the ^{95}Mo chemical shift is sensitive

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Table I. ^{95}Mo NMR and UV–Vis Spectroscopic Data for the *cis*-Mo(CO)$_4$(PPh$_2$XR)$_2$ and Mo(CO)$_4$(PPh$_2$YPPh$_2$) Complexes

cis-Mo(CO)$_4$(PPh$_2$XR)$_2$

	^{95}Mo^{a} NMR			UV–vis lowest energy absorption band^{b}	
XR	δ	$^1J_{\mathrm{MoP}}$, Hz	$\nu_{1/2}$, Hz	λ, nm	ε, L mol^{-1} cm^{-1}
Cl (**1**)	−1522	166	70	356	5000
NH$_2$ (**2**)	−1652	144	50	345	3000
NHMe (**3**)	−1622	138	100	348	2000
OMe (**4**)	−1707	153	40	337	8000
SEt (**5**)	−1540	140	150	357	5000
NHSiMe$_3$ (**6**)	−1563	139	80	352	3000
OSiMe$_3$ (**7**)	−1623	162	60	345 sh	3000
NHC$_6$H$_4$-*p*-Me (**8**)	−1571	140	80	351	2000
OC$_6$H$_4$-*p*-Me (**9**)	−1654	157	90	342 sh	5000
SC$_6$H$_4$-*p*-Me (**10**)	−1537	133	100	365	6000

Mo(CO)$_4$(PPh$_2$YPPh$_2$)

	^{95}Mo^{a} NMR			UV–vis lowest energy absorption band^{b}	
Y	δ	$^1J_{\mathrm{MoP}}$, Hz	$\nu_{1/2}$, Hz	λ, nm	ε, L mol^{-1} cm^{-1}
NHSiMe$_2$NH (**11**)	−1610	145	40	345	3000
OSiMe$_2$O (**12**)	−1700	154	90	335	5000
NHSiMe(Ph)NH (**13**)	−1676	144	60	342	4000
OSiMe(Ph)O (**14**)	−1685	155	50	337	4000
$^1/_2$O$_4$Si (**15**)	−1710	153	50	335	9000
NMeCH$_2$CH$_2$NMe (**16**)	−1670	153	60	345	3000

^{a} All resonances are triplets. Precision of measurement ±2 ppm. Measurements taken on saturated dichloromethane-d_2 solutions of the complexes. ^{b} Measurements taken on 1×10^{-5} M dichloromethane solutions. Precision of measurement ±2 nm except for shoulders (sh) where the measurement precision is ±5 nm.

to both the steric bulk[12] and σ-donor/π-acceptor ability[13] of the P-donor ligands in Mo(CO)$_5$(P-donor ligand)$_2$ complexes. In this study, the ^{95}Mo spectra of a series of Mo(CO)$_4$(P-donor ligand)$_2$ complexes, in which the steric and electronic properties of the P-donor ligands are allowed to vary more greatly than in previous studies, have been obtained. The relationship of the ^{95}Mo chemical shifts with the chemical shifts of the other resonances and with the UV–vis charge-transfer bands has been studied, and these are also discussed.

Experimental Section

Literature methods[14-16] were used to prepare all complexes used in this study except for *cis*-Mo(CO)$_4$(PPh$_2$SC$_6$H$_4$-*p*-Me)$_2$, which was prepared in 42% yield by using the procedure reported for *cis*-Mo(CO)$_4$(PPh$_2$OMe)$_2$.

Molybdenum-95 NMR spectra were taken of saturated dichloromethane-d_2 solutions of the complexes with use of a JEOL FX90Q multinuclear NMR spectrometer fitted with a 10-mm, low-frequency tunable probe insert and were referenced to an external 2 M aqueous Na$_2$MoO$_4$ solution at pH 11. The following parameters were used for spectra acquisition: frequency width, 5000 Hz; resolution, 10 Hz (512 data points); pulse width, 91 μs (90°); pulse delay, 40 ms; number of accumulations, 10^5–10^6. The ^{95}Mo NMR spectral data are summarized in Table I.

UV–vis spectra (450–250 nm) of 1×10^{-5} M dichloromethane solutions of the cis complexes used in this study were obtained with use of a Cary 219 UV–vis spectrophotometer in the auto slit mode. The UV–vis data are summarized in Table I.

Results and Discussion

^{95}Mo Spectra. The ^{95}Mo NMR spectra of the bis(P-donor ligand)tetracarbonylmolybdenum(0) complexes are 1:2:1 triplets found 1422–1738 ppm upfield of the Na$_2$MoO$_4$ reference, which is farther downfield than the resonances of other molybdenum carbonyl complexes of P-donor ligands.[9,11-13] The chemical shifts of the ^{95}Mo resonances appear to be a function of the type of P-donor ligand with the resonances of the complexes of phosphinite esters (Ph$_2$POR) found at highest field (−1676 to −1707 ppm) followed by the resonances of the complexes of phosphinamide ligands (Ph$_2$PNHR) (−1563 to −1676 ppm), the resonances of the complexes of thiophosphinite esters (Ph$_2$PSR) (−1537 to −1540 ppm), and finally the resonance of the chlorodiphenylphosphine (−1522 ppm). This order is not consistent with changes in the electronegativities of the XR groups but may be a function of the ability of these groups to donate π-electron density into the empty phosphorus d orbitals, reducing the back-donation of electron density from the molybdenum d orbitals into these orbitals and increasing the electron density at the molybdenum. This explanation is consistent with the observation that the ^{95}Mo resonances of the complexes in which the R group is an electron donor (Me) are further upfield than are those of the complexes in which the R group is an electron acceptor (C$_6$H$_4$-*p*-Me). It is also consistent with the fact that the ^{95}Mo resonances of the R = Me complexes are further upfield than are those of the R = SiMe$_3$ complexes since the silicon atoms also have empty d orbitals that can complete with those of the phosphorus for the electron density of the filled p orbitals of the X group. Such competition would result in a reduction of the electron density at the molybdenum via π-back-donation.[13]

The one problem with the above explanation of ^{95}Mo chemical shifts is that the third-row elements sulfur and chlorine might be expected to be better π-donors than the second-row elements oxygen and nitrogen since the phosphorus 3d orbitals would overlap better with the 3p orbitals than with the 2p orbitals. However, this effect may be countered by the empty 3d orbitals of the third-row elements, which would accept electron density from the phosphorus and reduce the overall π-electron-donor ability of the third-row elements.

The one-bond molybdenum–phosphorus coupling constants, $^1J_{\mathrm{MoP}}$, observed for the bis(P-donor ligand)tetracarbonylmolybdenum(0) complexes in this study are in the same range as those previously reported for other molybdenum carbonyl complexes containing PPh$_2$XR (X = O, NH; R = alkyl) ligands.[12,13] The $^1J_{\mathrm{MoP}}$ values of the X = O complexes (155–167 Hz) are significantly larger than those of the X = NH (138–145 Hz) and the X = S (133–140 Hz) complexes and approximately the same as that of the *cis*-Mo(CO)$_4$(PPh$_2$Cl)$_2$ complex (166 Hz). The magnitude of $^1J_{\mathrm{MoP}}$ appears to in-

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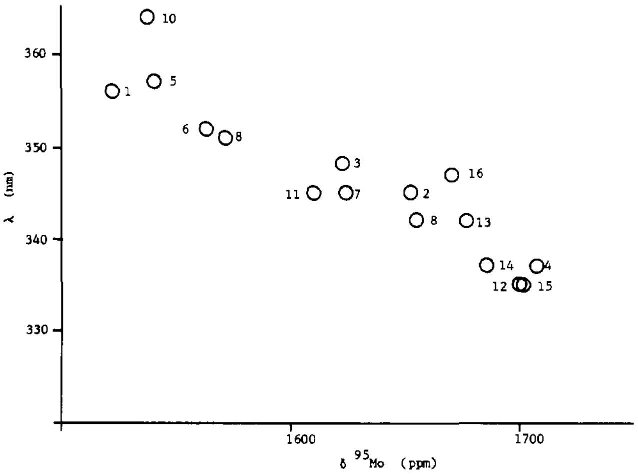

Figure 1. Plot of the ^{95}Mo NMR chemical shifts vs. the wavelengths of the highest frequency UV–vis charge-transfer bands for a series of *cis*-Mo(CO)$_4$(P-donor ligand)$_2$ complexes.

crease with the increasing electronegativity of the X group; i.e., $^1J_{MoP}$ for X = O, Cl is greater than that for X = NH, S.

The peak half-heights ($\nu_{1/2}$) of the ^{95}Mo resonances of the bis(P-donor ligand)tetracarbonylmolybdenum(0) complexes in this study range from 40 to 150 Hz. These somewhat large line widths have been attributed to the relatively large field gradient present at the ^{95}Mo nucleus of *cis*-bis(P-donor ligand)tetracarbonylmolybdenum(0) complexes[11] and are also similar in magnitude to those previously reported for some (diphenylphosphinamide)- and (diphenylphosphinite)pentacarbonylmolybdenum(0) complexes.[12,13]

^{95}Mo Chemical Shift Correlations. The correlations observed between the ^{95}Mo chemical shifts and the other chemical shifts in these complexes are uniformly poor. These poor correlations were expected as earlier studies of Mo(CO)$_5$(PPh$_2$XR) (X = NH or O, R = alkyl;[12] X = O, R = para-substituted phenyl[13]) complexes have demonstrated that good correlations involving the ^{95}Mo chemical shifts are only observed when the steric and electronic changes in the P-donor ligands are carefully controlled. This is reflected in the improvement in the correlation between ^{95}Mo and ^{31}P chemical shifts when the data used for the correlation are reduced from those for all the complexes ($r = -0.53$) to those for the complexes containing monodentate ligands with similar cone angles (complexes **3**–**10**, $r = -0.88$).

Although poor correlations are observed between the chemical shifts of the ^{95}Mo resonances and all other resonances, a good correlation ($r = 0.93$) is observed between the chemical shifts of the ^{95}Mo resonances and the wavelength of the lowest frequency optical absorption maxima of the neutral complexes of monodentate ligands and of bidentate ligands that form six- or seven-membered rings, compounds **1**–**16**, as shown in Figure 1. This correlation is similar to those previously reported between the wavelength of the lowest frequency visible absorptions and the ^{59}Co NMR chemical shifts for two series of cobalt(III) complexes,[17,18] the ^{183}W NMR chemical shifts of a series of polytungstates,[19] and the ^{95}Mo NMR chemical shifts of a series of dioxomolybdenum(VI) Schiff base complexes.[8]

These correlations between the lowest frequency optical absorption maxima and heavy-metal NMR chemical shifts have been ascribed to the domination of heavy-metal shielding by the paramagnetic term of Ramsey's treatment of chemical shielding.[20-25] This is given approximately by eq 1, where ΔE is an average energy of electronic excitation from the ground

$$\sigma^P = -(2e^2h^2/3m^2c^2\Delta E)(\langle r^{-3}\rangle_{np}P_i + \langle r^{-3}\rangle_{nd}D_i) \quad (1)$$

state to states that are of the correct symmetry and are mixed in by the magnetic field, $\langle r^{-3}\rangle_{np}$ and $\langle r^{-3}\rangle_{nd}$ are radial expression terms representing the average inverse cubes of the distances of the relevant p and d electrons, and P_i and D_i are measures of the degree of electronic imbalance in the relevant p and d orbitals. Since ΔE can often be related to the wavelength of the lowest frequency visible absorption, a linear correlation should be observed between the chemical shifts and these wavelengths within a series of complexes as long as the other terms, $\langle r^{-3}\rangle_{np}$, $\langle r^{-3}\rangle_{nd}$, P_i, and D_i, remain approximately constant for the series.

Conclusions

From the study of the ^{95}Mo NMR spectra of a series of *cis*-Mo(CO)$_4$(PPh$_2$XR)$_2$ complexes, an explanation of the effect of changes in the XR groups on the ^{95}Mo chemical shifts has been proposed that involves π-donation from the filled p orbitals of the X group into the empty phosphorus 3d orbitals. This study has also demonstrated that although the chemical shifts of the ^{95}Mo resonances do not correlate with the chemical shifts of other resonances of the complexes, a good correlation is obtained with the wavelengths of the highest frequency UV–vis absorption band. This correlation can be related to the paramagnetic term of Ramsey's treatment of chemical shielding.

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Registry No. **1**, 42724-61-8; **2**, 55835-45-5; **3**, 66024-56-4; **4**, 65991-64-2; **5**, 65991-51-7; **6**, 86707-60-0; **7**, 65991-54-0; **8**, 65991-63-1; **9**, 65991-50-6; **10**, 86646-33-5; **11**, 65614-05-3; **12**, 65991-55-1; **13**, 65991-45-9; **14**, 65991-56-2; **15**, 65991-57-3; **16**, 73643-89-7.

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Wavelength Independence of Phosphorescence Yields in [Cr(en)$_3$]$^{3+}$

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There have been several reports in the literature that for particular chromium(III) complexes there is a wavelength dependence of the intersystem crossing yield on irradiation within a single absorption band. Such studies have been based on either measurements of the percentage of quenchable photoreaction or measurements of relative phosphorescence yields from the metastable doublet state,[2-4] and in one recent

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