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# Bonding Properties of $Mo(CO)_{4-x}L(PR_3)_x$ (x = 0, 1, 2; L = diazabutadiene, pyridine-2-carbaldehyde imine and 2,2′-bipyridine). Infrared, Electronic Absorption, $^1$H, $^{13}$C and $^{31}$P NMR and Resonance Raman Spectra

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*Infrared and electronic absorption, $^1$H, $^{13}$C and $^{31}$P NMR and resonance Raman spectra of the complexes $Mo(CO)_4L$, $Mo(CO)_3L(PR_3)$ and $Mo(CO)_2L(PEt_3)_2$ (L = 1,4-diazabutadiene, pyridine-2-carbaldehyde imine and 2,2′-bipyridine; R = $OCH_3$, $C_6H_5$, $C_2H_5$, $C_4H_9$, c-$C_6H_{11}$) are reported. The π-backbonding between Mo and L appears to be much stronger for L = DAB than for the other two ligands. The influences of basicity and bulkiness of the $PR_3$ group on the bonding properties of the complexes are discussed.*

*Several Mo to L CT bands are observed and assigned. The character of these bands and the properties of the excited states are investigated with the use of the resonance Raman effect.*

*The absorption spectra of some of the complexes show drastic changes in low temperature alkane glasses.*

## Introduction

During the last few years much attention has been paid in our laboratory to the coordinating properties of nitrogen bases with cumulated double bonds. In this respect, ligands containing the sulfurdiimine (N=S=N) group have been investigated in detail. Alkylsulfurdiimines with large alkylgroups such as di-t-butylsulfurdiimine (DBSD) appear to coordinate to $Cr^0$, $Mo^0$ and $W^0$ as bidentate ligands. The bonding properties of $Mo(CO)_4$DBSD have been discussed [1] and compared with the results of other $Mo(CO)_4L$ compounds.

A close analogy exists between $Mo(CO)_4$DBSD and $Mo(CO)_4$DAB (DAB = 1,4-diazabutadiene) of which the latter compounds have been studied by tom Dieck *et al.* [2–6]. Both types of complexes show very intense solvatochromic CT bands in the visible region. The conclusion that a strong π-backbonding between Mo and the bidentate ligand exists, prompted us to investigate in more detail the bonding properties of a series of $Mo(CO)_4L$ compounds in which L represents a bidentate nitrogen base with conjugated double bonds. In a previous article [7] the spectroscopic properties of some $Mo(CO)_4$DAB complexes have been described. In this paper we present a comparative study of $Mo(CO)_4L$ compounds in which L represents DAB (I), pyridine-2-carbaldehyde imine (II) and 2,2′-bipyridine (III). Furthermore, the influence of basicity and steric hindrance of phosphine groups on the bonding properties of $Mo(CO)_3L(PR_3)$ and $Mo(CO)_2L(PEt_3)_2$ is discussed.

## Experimental

### *Preparations*

The tetra- and dicarbonyls $Mo(CO)_4L$ and $Mo(CO)_2L(PEt_3)_2$, with L = i-$C_3H_7$–N=CH–CH=N–i-$C_3H_7$ (DAB), i-$C_3H_7$–N=CH-2-$C_5H_4N$ (PyCa) and 2,2′-bipyridine (bipy) were prepared by standard methods [8, 10]. The tricarbonyls $Mo(CO)_3L(PR_3)$, with R = $OCH_3$, $C_6H_5$, $C_4H_9$ and c-$C_6H_{11}$ were all prepared from their corresponding tetracarbonyls.

All compounds are very intensively coloured. Some tri- and dicarbonyls are very sensitive to air, and have to be kept at −10 °C. In solution all compounds are photochemically labile. When heated under CO atmosphere the phosphine-substituted carbonyls do not show any reaction. Most of them decompose above 100 °C. Some compounds sublimed *in vacuo* above 100 °C.

### *Physical Measurements*

Dipole measurements were carried out on a General Radio "Capacitance-Measuring Assembly" type 1620 A, with 1–4 × $10^{-3}$ *M* benzene solutions of $Mo(CO)_4$DAB and $Mo(CO)_4$PyCa, and with 0.5–1,25 × $10^{-3}$ *M* benzene solutions of $Mo(CO)_4$bipy.

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TABLE I. Elemental Analyses.[a]

| $Mo(CO)_4L$ | | $C^{exp.}$ | $C^{calc.}$ | $H^{exp.}$ | $H^{calc.}$ | $N^{exp.}$ | $N^{calc.}$ |
|---|---|---|---|---|---|---|---|
| DAB | | 41.50 | 41.39 | 4.72 | 4.64 | 8.05 | 7.90 |
| PyCa | | 43.72 | 43.83 | 3.39 | 3.40 | 7.72 | 7.87 |
| bipy | | 46.42 | 46.17 | 2.31 | 2.21 | 7.62 | 7.69 |
| $Mo(CO)_3L(PR_3)$ | | | | | | | |
| DAB | $P(OMe)_3$ | 37.89 | 37.85 | 5.98 | 5.67 | 6.25 | 6.31 |
| | $P\phi_3$ | 59.0 | 59.79 | 5.46 | 5.36 | 4.59 | 4.81 |
| | $PEt_3$ | 45.9 | 46.58 | 7.25 | 7.13 | 6.12 | 6.39 |
| PyCa | $P(OMe)_3$ | 39.27 | 39.83 | 4.79 | 4.68 | 5.90 | 6.20 |
| | $P\phi_3$ | 60.99 | 61.02 | 4.56 | 4.61 | 4.58 | 4.75 |
| | $PEt_3$ | 47.8 | 48.44 | 6.06 | 6.10 | 6.05 | 6.28 |
| | $PBu_3$ | 53.7 | 54.34 | 7.45 | 7.41 | 4.95 | 5.28 |
| | $PCy_3$ | 58.6 | 59.20 | 7.50 | 7.45 | 4.79 | 4.60 |
| bipy | $P(OMe)_3$ | 41.52 | 41.75 | 3.99 | 3.72 | 5.85 | 6.09 |
| | $P\phi_3$ | 62.22 | 62.22 | 4.00 | 3.87 | 4.61 | 4.68 |
| | $PEt_3$ | 49.5 | 50.23 | 5.15 | 5.10 | 6.16 | 6.17 |
| | $PBu_3$ | 55.69 | 55.76 | 6.69 | 6.55 | 5.24 | 5.20 |
| $Mo(CO)_2L(PEt_3)_2$ | | | | | | | |
| DAB | | 48.78 | 50.00 | 8.73 | 8.77 | 5.09 | 5.30 |
| PyCa | | 50.80 | 51.49 | 7.77 | 7.89 | 5.37 | 5.22 |
| bipy | | 52.01 | 52.94 | 7.15 | 7.04 | 5.07 | 5.15 |

[a] Some compounds retained solvent molecules in their crystals, even after hours of evaporation. This appeared also from NMR spectra. No good analyses could be obtained for these compounds.

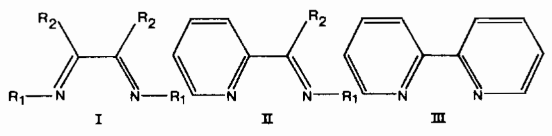


Figure 1. Three types of α-diimine ligands.

The evaluation of the dipole moments was carried out according to Higasi's method for dilute solutions.

The electronic absorption spectra were recorded on a Cary 14 spectrophotometer, the infrared spectra with Beckman IR 4250 and IR 12 spectrophotometers.

Resonance Raman spectra were recorded with a Coderg PH 1 spectrometer and excited by Argon CR 8, Krypton CR 500 K lasers and by a tunable dye-laser model CR 490 with Rhodamine-B and 110 as dyes, from 647 to 458 nm. The spectra were recorded with a cooled (−10 °C) spinning cell from $1–8 \times 10^{-4}$ $M$ solutions in chloroform and carbon disulfide, while the 758 $cm^{-1}$ band of $CHCl_3$ and the 397 $cm^{-1}$ band of $CS_2$ were used as internal standards. Corrections were applied for the sensitivity of the spectrophotometer, the absorption of the scattered light and decomposition in the laser beam.

$^1H$ NMR spectra were recorded with Varian T60 and A60 spectrometers; $^{13}C$ NMR spectra with Varian CFT-20 and $^{31}P$ NMR spectra with Varian XL-100 spectrometers. The C, H and N analyses were carried out at the micro-analysis laboratory of TNO in Utrecht, and are listed in Table I.

## Results and Discussion

### Vibrational Spectra

*$Mo(CO)_4L$*

The CO stretching modes of the $Mo(CO)_4L$ compounds under discussion are presented in Table II together with the results for $Mo(CO)_4en$ (en = ethylenediamine) and $Mo(CO)_4(CH_3CN)_2$.

These latter compounds have no π-backbonding from Mo to ethylenediamine or $CH_3CN$ respectively and their ν(CO) frequencies are therefore low.

Higher frequencies are found for the $Mo(CO)_4L$ compounds (with L = I, II or III) indicating the presence of π-backbonding from Mo to L. Comparing the results for the three ligands L, we can conclude that DAB has a much stronger π-interaction with Mo than bipy and PyCa. This conclusion is confirmed by the lowering of ν(CN) for DAB and PyCa with respect to the free ligands. For DAB this lowering is about 100 $cm^{-1}$, for PyCa only 30 $cm^{-1}$. The dipole moments of the compounds agree with these results. The bipy and PyCa complexes have nearly the same dipole moment which is much higher than for the DAB compound.

TABLE II. IR Spectral Results (in $cm^{-1}$).

| | | $\mu$(D)[a] | $\nu$(C≡O)[b] | | | | | $\nu$(C=N)[c] | | Py Modes[c,d] | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | I | II | III | IV |
| $Mo(CO)_4en$[e] | | | 2015 | | 1890 | 1864 | 1818 | | | | | | |
| $Mo(CO)_4(CH_3CN)_2$[f] | | 9.7 | 2023 | | 1912 | 1881 | 1833 | | | | | | |
| DAB | | | | | | | | 1629 | | | | | |
| $Mo(CO)_4DAB$ | | 8.2 | 2014 | | 1915 | 1894 | 1841 | 1532 | | | | | |
| $Mo(CO)_3DAB$ | $P(OMe)_3$ | | | 1935 | | 1846 | 1810 | 1486 | | | | | |
| | $P\Phi_3$ | | | 1929 | | 1840 | 1807 | 1479 | | | | | |
| | $PEt_3$ | | | 1925 | | 1836 | 1806 | 1478 | | | | | |
| | $PBu_3$ | | | 1926 | | 1834 | 1808 | 1460 | | | | | |
| | $PCy_3$ | | | 1923 | | 1833 | 1805 | 1452 | | | | | |
| $Mo(CO)_2DAB$ | $(PEt_3)_2$ | | | | | 1858 | 1762 | 1493 | | | | | |
| PyCa | | | | | | | | 1645 | | 1588 | 1567 | 1468 | 1436 |
| $Mo(CO)_4PyCa$ | | 9.7 | 2013 | | 1905 | 1883 | 1832 | 1612 | | 1585 | 1556 | 1470 | 1442 |
| $Mo(CO)_3PyCa$ | $P(OMe)_3$ | | | 1929 | | 1834 | 1798 | 1607 | | 1584 | 1551 | 1465 | – |
| | $P\Phi_3$ | | | 1919 | | 1823 | 1794 | 1608 | | 1584 | 1546 | 1465 | – |
| | $PEt_3$ | | | 1913 | | 1814 | 1790 | 1604 | | 1587 | 1544 | 1464 | 1440 |
| | $PBu_3$ | | | 1913 | | 1812 | 1790 | 1605 | | 1587 | 1545 | 1466 | 1441 |
| | $PCy_3$ | | | 1907 | | 1805 | 1785 | 1606 | | 1589 | 1548 | 1467 | 1440 |
| $Mo(CO)_2PyCa$ | $(PEt_3)_2$ | | | | | 1822 | 1739 | | 1590 | | 1547 | – | – |
| bipy | | | | | | | | | | 1585 | 1562 | 1456 | 1421 |
| $Mo(CO)_4bipy$ | | 10.1 | 2008 | | 1905 | 1877 | 1830 | | | 1598 | 1566 | 1469 | 1440 |
| $Mo(CO)_3bipy$ | $P(OMe)_3$ | | | 1924 | | 1826 | 1790 | | | 1598 | 1566 | 1467 | 1442 |
| | $P\Phi_3$ | | | 1916 | | 1819 | 1789 | | | 1597 | – | 1465 | – |
| | $PEt_3$ | | | 1909 | | 1806 | 1782 | | | 1594 | – | 1465 | 1441 |
| | $PBu_3$ | | | 1908 | | 1805 | 1783 | | | 1597 | – | 1462 | 1436 |
| | $PCy_3$ | | | 1903 | | 1798 | 1777 | | | 1598 | – | 1464 | 1438 |
| $Mo(CO)_2bipy$ | $(PEt_3)_2$ | | | | | 1796 | 1719 | | | 1586 | 1540 | 1460 | – |

[a] Measured in benzene at 25.6 °C. [b] Recorded in dichloromethane. [c] In Kel-F muls. [d] Nomenclature from ref. 11. [e] Ref. 12. [f] Ref. 13, 14.

The similarity between the π-interaction of Mo with bipy and PyCa indicates that pyridine orbitals much more contribute to the lowest excited state of PyCa than orbitals of the C=N group. This assumption is confirmed by the resonance Raman spectra which are discussed below.

### *$Mo(CO)_3L(PR_3)$ and $Mo(CO)_2L(PEt_3)_2$*

Substitution of CO by $PR_3$ which takes place at a *cis*-position with respect to L [2, 10], causes a lowering of ν(CO). This lowering depends on R according to the following series: $P(OMe)_3 < P\Phi_3 < PEt_3 \sim PBu_3 < PCy_3$. The $PR_3$ groups appear to be arranged in order of increasing basicity, in agreement with the results of Barbeau for $Mo(CO)_{6-n}(PR_3)_n$ (n = 1, 2, 3) [13]. No large steric influence is observed here because the results do not agree with the order of increasing cone angle for these $PR_3$ groups which has been calculated by Tolman: $P(OMe)_3 < PEt_3 \sim PBu_3 < P\Phi_3 < PCy_3$ [15, 16].

Comparing the results for the three ligands L, the frequency lowering of ν(CO) with respect to $Mo(CO)_4L$ increases from DAB < PyCa < bipy. This result again demonstrates the stronger π-backbonding from Mo to DAB with respect to the other two ligands. It agrees with the large influence of substitution of CO by $PR_3$ on the $\nu_s$(CN) frequency of DAB (~60 $cm^{-1}$) with respect to PyCa (~6 $cm^{-1}$). Substitution of a second CO group by $PEt_3$ also occurs at the *cis*-position with respect to L [9] and causes a further lowering of ν(CO).

The influence of substitution of CO by $PEt_3$ on the π-backbonding between Mo and L is nicely shown by the frequency shifts of the CN and Py modes of the ligands L (see Table II). Going from $Mo(CO)_4L$ to $Mo(CO)_3L(PEt_3)$ these frequencies are lowered, indicating a strengthening of the Mo to L backbonding for all three ligands L. From $Mo(CO)_3L(PEt_3)$ to $Mo(CO)_2L(PEt_3)_2$ a small lowering of frequency is observed for the PyI and PyIII modes of bipy and for the ν(CN) of PyCa. On the other hand, for L = DAB and PyCa a shift to higher frequency is found for the $\nu_s$(CN) vibration of DAB and the PyII mode of PyCa. This means that substitution of a

TABLE III. UV Spectral Results (Energies in kK).

| | Metal–LCT transitions | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $b_2^* \leftarrow a_1$ | $b_2^* \leftarrow b_2$ | $b_2^* \leftarrow a_2$ | $a_2^* \leftarrow a_1$ | $a_2^* \leftarrow b_2$ | $a_2^* \leftarrow a_2$ | d ← d | $\Delta^{a}_{b_2^* \leftarrow b_2}$ | $\Delta^{a}_{a_2^* \leftarrow a_2}$ |
| L = DAB | | | | | | | | | |
| $Mo(CO)_4L$* | | 17.8 | 19.1 | | | | 27.1 | 2.2 | |
| $Mo(CO)_3L\{P(OMe)_3\}$ | 15.2 | 17.5 | 19.4 | 21.3 | | | 29.1 | 0.8 | |
| $P\Phi_3$ | (15.6[d]) | 17.0 | (19.3[d]) | | | | 27.6 | 0.9 | |
| $PEt_3$ | | 17.3 | | | | | 28.6 | 0.1 | |
| $PBu_3$ | | 17.2 | | | | | 29.0 | 0 | |
| $PCy_3$ | | 17.6 | 16.9 | | | | 28.7 | –0.1 | |
| $Mo(CO)_2L\ (PEt_3)_2$ | 15.4 | 19.7 | 17.2 | | | | 25.3 | –0.4 | |
| L = PyCa | | | | | | | | | |
| $Mo(CO)_4L$* | | 17.4 | 19.1 | 21.0 | | | 26.3 | 3.9 | |
| $Mo(CO)_3L\{P(OMe)_3\}$ | | 16.4 | 18.0 | 19.5 | | 24.2 | 27.9 | 2.7 | (4.1) |
| $P\Phi_3$[b] | (15.5[d]) | 16.0 | 18.0 | | | | – | 2.4 | |
| $PEt_3$* | | 15.2 | 17.2 | 19.3 | | 22.6 | 27.7 | 2.4 | 4.8 |
| $PBu_3$* | | 15.0 | 16.3 | | | 22.5 | 27.7 | 2.4 | 4.7 |
| $PCy_3$ | (15.0[e]) | 15.3 | 17.4 | 19.2 | | 22.3 | 27.2 | 2.2 | 5.2 |
| $Mo(CO)_2L\ (PEt_3)_2$ | | 14.9 | | | 19.0 | 20.6 | 25.5 | –0.5 | 0.7 |
| L = bipy | | | | | | | | | |
| $Mo(CO)_4L$[b] | | 18.5 | 20.7 | | | | 25.2 | 4.1 | |
| $Mo(CO)_3L\{P(OMe_3)\}$[c] | | 17.1 | | | | 24.4 | 27.2 | 3.1 | (3.7) |
| $P\Phi_3$[b] | (16.4[d]) | 16.1 | 18.2 | | | | – | 3.3 | |
| $PEt_3$[c] | | 15.2 | | | | 22.8 | 27.5 | 3.5 | 4.4 |
| $PBu_3$[c] | | 15.1 | | | | 22.6 | 27.5 | 3.3 | 4.6 |
| $PCy_3$[b] | | 15.0 | | | | 22.7 | – | 3.5 | 4.7 |
| $Mo(CO)_2L\ (PEt_3)_2$* | | 12.0 | 13.4 | 14.9 | 17.5 | 19.0 | 25.1 | 1.6 | 2.1 |

Spectra were recorded in cyclohexane.

[a] $\Delta \equiv (\sigma_{CH_3CN} - \sigma_{c\text{-}C_6H_{11}})^{max}$. [b] Recorded in carbon disulphide and. [c] in carbon tetrachloride. [d] At –160 °C in diethylether/ethanol/toluene. [e] In acetonitrile solution. *Compounds whose spectra show drastic changes when cooled in alkane solutions.

second CO group by $PEt_3$ causes a small increase of overlap between metal d and $L\pi^*$ orbitals when L = bipy and still when L = PyCa, but a decrease when L = DAB.

This result is in close agreement with the absorption spectra of these compounds (*vide infra*).

### *Electronic Absorption Spectra*

Some typical spectra of the complexes are shown in Figures 2 and 3; the results are presented in Table III. Only the bands in the visible region are shown and will be discussed here. Apart from a weak LF band between 350–400 nm a solvatochromic band is always present at longer wavelength. The solvatochromic behaviour of this band has been discussed by tom Dieck *et al.* for the $Mo(CO)_{4-x}DAB(PR_3)_x$ compounds (x = 0, 1, 2) [17, 18]. They assigned the band to a z-polarized metal to DAB CT transition. It is however clear from *e.g.* figure 2a that this band is structured which effect becomes more pronounced at lower temperature. Recently Staal *et al.* [7] have investigated the structure of such a CT band for a $Mo(CO)_4DAB$ compound. They assigned the subbands to different metal to DAB CT transitions with the use of resonance Raman results.

In principle six of these transitions can occur as shown in Figure 4b which represents the relevant part of a tentative MO diagram for the $Mo(CO)_4DAB$ compounds. One of these transitions ($a_2^* \leftarrow a_1$) is symmetry forbidden for molecules with $C_{2v}$ symmetry, a second one ($b_2^* \leftarrow a_1$) is overlap forbidden and is therefore expected to be very weak. The same result is expected for the corresponding complexes of PyCa and bipy, although this $C_{2v}$ symmetry is partially distorted in $Mo(CO)_4PyCa$. The influence of this distortion on the transition probabilities however, will be small.

In agreement with the assignments of tom Dieck [17, 18] and Staal [7] the strongest band is assigned to the z-polarized $b_2^* \leftarrow b_2$ transition. The shoulder at the high energy side of this band which shows up

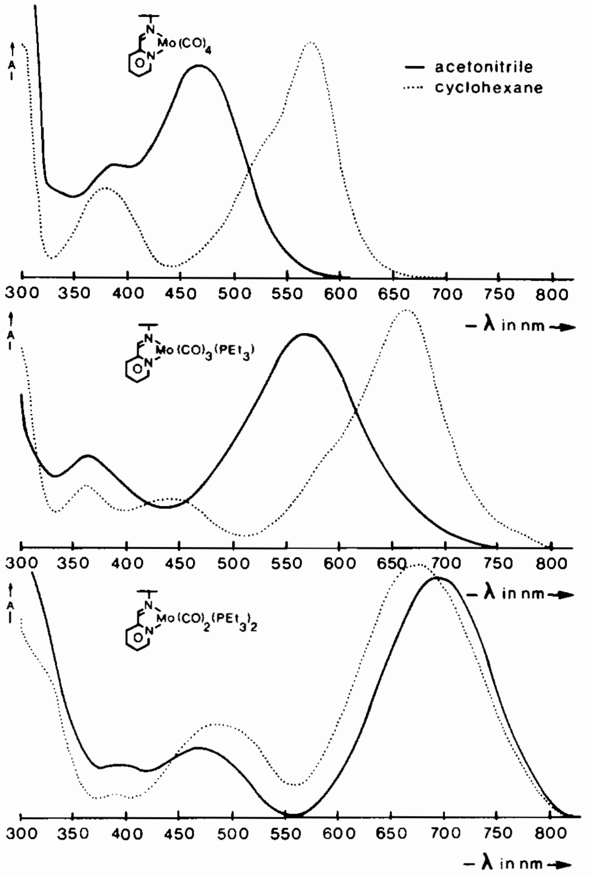


Figure 2. Solvatochromism of $Mo(CO)_{4-x}PyCa(PEt_3)_x$ (x = 0, 1, 2).

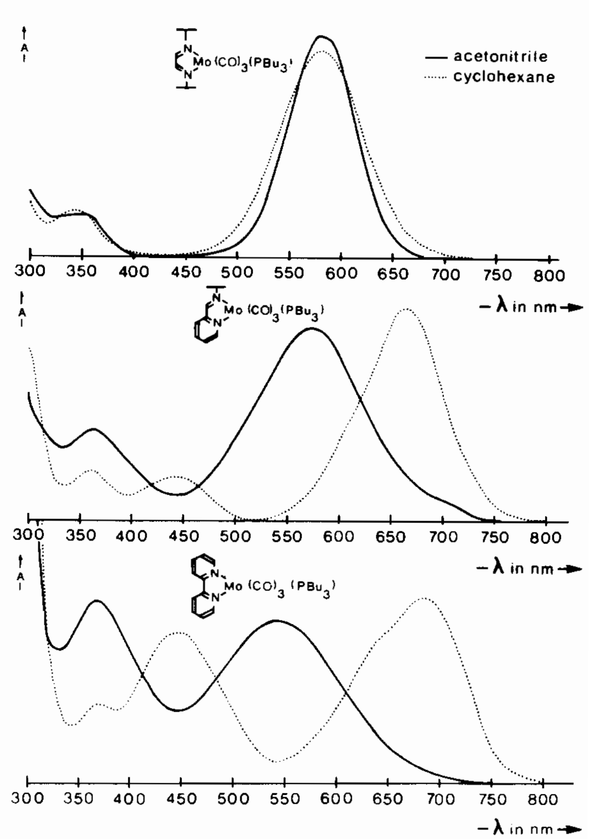


Figure 3. Solvatochromism of $Mo(CO)_3L(PBu_3)$ (L = DAB, PyCa, bipy).

in apolar solvents and at lower temperatures is assigned to the x-polarized $b_2^* \leftarrow a_2$ transition.

Nearly all complexes possess a very weak shoulder at the low energy side of the $b_2^* \leftarrow b_2$ transition, which becomes more pronounced at lower temperatures and which is assigned to the y-polarized, overlap forbidden $b_2^* \leftarrow a_1$ transition. Transitions to the $a_2^*$ orbital of the ligand L (see figure 4) can hardly be detected for the $Mo(CO)_4L$ compounds. For $Mo(CO)_4PyCa$ a weak shoulder is observed at about 21 kK, which is tentatively assigned to the $a_2^* \leftarrow a_1$ transition. Such a weak shoulder has also been observed by Staal [7] for a $Mo(CO)_4DAB$ compound. Furthermore, the spectrum of $Mo(CO)_4PyCa$ in $CH_3CN$ (figure 2a) possesses a shoulder at the high energy side of the LF band, which is not observed in the spectrum of this compound in cyclohexane. This indicates the presence of a second solvatochromic band, which is therefore assigned to the z-polarized $a_2^* \leftarrow a_2$ transition. Strong evidence for this assignment is the appearance of such a solvatochromic band at the low energy side of the LF band in the phosphine substituted PyCa complexes (figures 2b, c). The same band is observed in the spectra of the phosphine substituted bipy complexes (figure 3c) [2] but has never been observed in any spectrum of a DAB compound. Figures 3b and 3c show that this band strongly increases in intensity going from PyCa to bipy. It is therefore assumed that this transition is too weak for the DAB compounds to be observed.

At the low-energy side of the $a_2^* \leftarrow a_2$ transition a shoulder is found in the spectra of $Mo(CO)_2PyCa(PEt_3)_2$ and $Mo(CO)_2bipy(PEt_3)_2$, which is assigned to the $a_2^* \leftarrow b_2$ transition. The transitions $a_2^* \leftarrow a_2$ and $a_2^* \leftarrow b_2$ possess the same difference in energy as the $b_2^* \leftarrow b_2$ and $b_2^* \leftarrow a_2$ transitions.

Substitution of CO by $PR_3$ has a large influence on the positions of the bands. Introduction of such a group destabilizes the metal d-orbitals. The bands are therefore expected to shift to lower energy until metal and ligand $b_2$ orbitals have the same energy. A further destabilization of metal d-orbitals by introduction of a second $PR_3$ group may cause a shift to higher energy. This is observed for the $Mo(CO)_{4-x}DAB(PEt_3)_x$ complexes.

Table III shows that the shift to lower energy increases with increasing basicity of the $PR_3$ group. This result agrees with the influence of $PR_3$ on the frequencies of the CO stretching modes, which has been discussed before. Although steric interaction

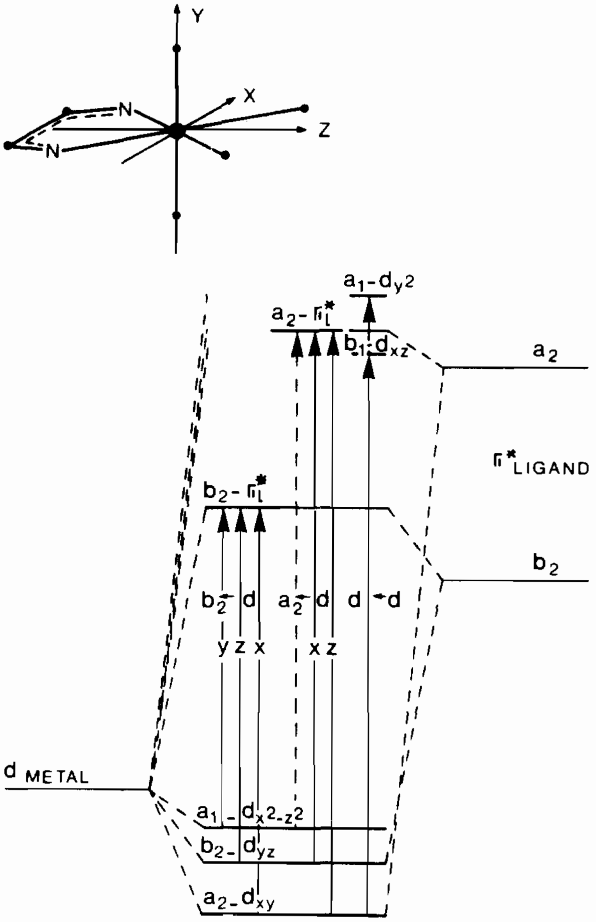


Figure 4. a) Direction of x, y and z axes in molecules with $C_{2v}$ symmetry. b) Relevant part of the M.O. diagram; possible transitions and polarization characteristics are shown.

between $PR_3$ group and ligands could not be observed in the IR spectra, it appears to be present because it has a pronounced effect on the spectra of Mo$(CO)_3$DAB$(P\Phi_3)$ and Mo$(CO)_3$DAB$(PCy_3)$. This is evident from the large shift to lower energy and solvatochromism of the $b_2^* \leftarrow b_2$ transition of these complexes due to a smaller overlap between the metal d orbitals and the $\pi^*$-ligand orbitals.

The influence of introduction of one $PR_3$ group, *e.g.* $PBu_3$, on the spectra greatly differs for the DAB compounds with respect to PyCa and bipy. The $b_2$ orbitals of the metal and DAB ligand become more strongly mixed when CO is replaced by $PR_3$ and as a result the metal to DAB transition looses its CT character and the solvatochromism of the band will disappear.

The corresponding transitions of the PyCa and bipy compounds remain CT in character and still show solvatochromism. The effect is nicely demonstrated in figure 3, and closely agrees with the IR results.

The increasing overlap between metal and DAB $b_2$ orbitals also influences the relative positions of the filled $b_2$ and $a_2$ orbitals. In Mo$(CO)_4$DAB the $b_2^* \leftarrow a_2$ transition is found at the high energy side of the $b_2^* \leftarrow b_2$ transition. Both transitions coincide for Mo$(CO)_3$DAB$(PBu_3)$ (see figure 3a). On the contrary for Mo$(CO)_2$DAB$(PEt_3)_2$ the $b_2^* \leftarrow a_2$ transition is observed at the low-energy side of the $b_2^* \leftarrow b_2$ transition. Apparently, substitution of CO by $PR_3$ in the DAB complexes stabilizes the filled $b_2$ orbitals with respect to $a_2$.

Contrary to the Mo$(CO)_4$L compounds the $b_2^* \leftarrow b_2$ transition of Mo$(CO)_2$DAB$(PEt_3)_2$ and Mo$(CO)_2$PyCa$(PEt_3)_2$ shows a red shift in polar solvents (figure 2c). This means that this band belongs to a ligand to metal CT transition. The metal $b_2$ orbital is raised above the $b_2^*$ orbital of the ligand. The $a_2^* \leftarrow a_2$ transition however, still corresponds to a metal to ligand CT transition and shows a blue shift in polar solvents. This is observed for Mo$(CO)_2$PyCa$(PEt_3)_2$ (figure 2c).

### *Low-temperature absorption spectra in alkane glasses*

Low-temperature spectra of some of these compounds in alkane glasses show drastic changes when the glassy solid is formed. The intense CT band disappears and a new structured band shows up at higher energy. At the same time the structure of the band becomes more pronounced.

This effect which has been observed for the first time for the M$(CO)_4$DAB complexes by Staal *et al.*

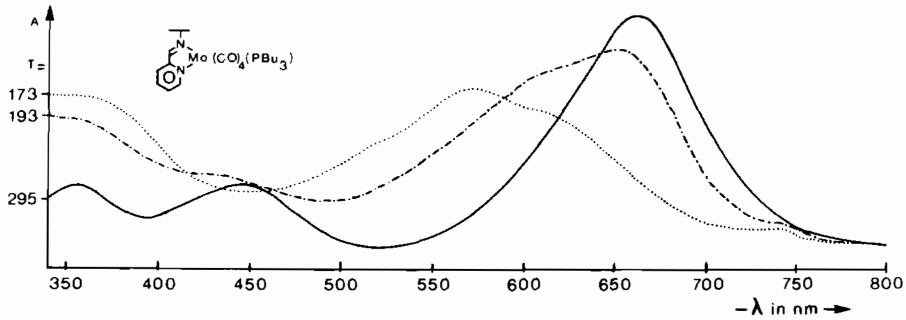


Figure 5. Low temperature UV spectra of Mo$(CO)_3$PyCa$(PBu_3)$ in rigisolve (a 8:3 mixture of 2,2-dimethylbutane and n-pentane).

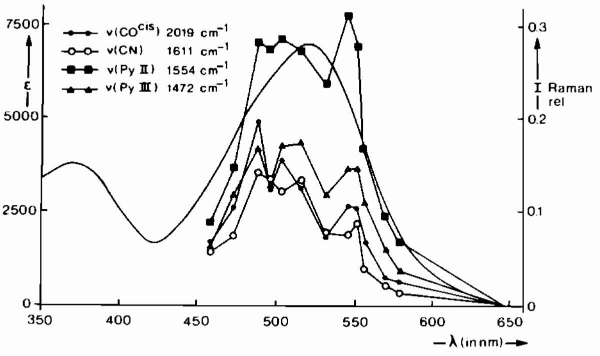


Figure 6. Excitation profiles of $Mo(CO)_4PyCa$ in $CHCl_3$, relative to the 758 cm$^{-1}$ band of $CHCl_3$.

[7a] only occurs in glasses of alkanes and mixtures of alkanes. A typical spectrum is shown in Figure 5.

The effect shows up for compounds with a high dipole moment in the direction of the z-axis (see Figure 4a) for DAB complexes with bulky $R_1$ groups and for some PyCa and bipy complexes. The compounds showing this effect are indicated with an asterisc in Table III. For a further discussion see ref. 7a.

### *Resonance Raman Spectra*

In order to get more information about the character of these CT transitions the resonance Raman spectra of $Mo(CO)_4PyCa$ and $Mo(CO)_3PyCa(PBu_3)$ were investigated.

#### *Mo(CO)$_4$PyCa*

Strong resonance enhancement of Raman intensity is found for $\nu$(PyII), $\nu$(PyIII) and $\nu$(C=N) of the PyCa ligand and for the symmetrical stretching mode of the *cis*-carbonyls $\nu_s(CO^{cis})$. All four vibrations are polarized. The structured absorption band therefore belongs to CT transitions to an excited state in which not only PyCa orbitals but also orbitals of the *cis* carbonyls are involved.

This effect which has also been observed for $M(CO)_4DBSD$ [1] and $M(CO)_4DAB$ [7] cannot be attributed to a mixing of PyCa and CO modes in the complex because introduction of $^{15}N$ in such a bidentate ligand does not influence the CO frequencies [7].

The excitation profiles, shown in Figure 6, do not completely coincide with the absorption band. This effect may be caused by interference between the amplitudes of preresonant and more nearly resonant states [19]. The excitation profiles show three maxima which correspond to three electronic transitions. These maxima nearly coincide for all four vibrations indicating that the subbands belong to different electronic transitions and not to a vibrational progression as has been observed by Clark *et al.* for $[Fe(DAB)_3]^{2+}$ systems [20].

The resonance enhancement is larger for the $\nu$(PyII) and $\nu$(PyIII) vibrations than for $\nu$(C=N) which indicates that pyridine orbitals most contribute to the lowest excited state of PyCa, in agreement with the IR and UV spectral results.

It has been shown that the strong long wavelength subband belongs to the z-polarized $b_2^* \leftarrow b_2$ transition. For this transition a resonance effect is expected for $\nu_s$(Mo–N) just as has been observed for $Mo(CO)_4$-DAB.

No such effect could be observed for a low-frequency mode of this compound in $CHCl_3$ presumably because of coincidence with a solvent band.

In $CH_3CN$ resonance enhancement is found for a weak polarized band at 242 cm$^{-1}$, which is assigned to $\nu_s$(Mo–N). The resonance effect is only found when excitation occurs at the long wavelength side of the absorption band. The long-wavelength maximum of the excitation profiles at about 550 nm will therefore certainly belong to the $b_2^* \leftarrow b_2$ z-polarized transition.

#### *Mo(CO)$_3$PyCa(PBu$_3$)*

This compound was chosen because we could excite here with the laser beam within the $a_2^* \leftarrow a_2$ transition of the complex at about 450 nm. Resonance enhancement was found for more vibrations than in the case of $Mo(CO)_4PyCa$, especially in the low-frequency region. Two $\nu_s$(Mo–C) [21] stretching modes at 432 cm$^{-1}$ and 466 cm$^{-1}$ respectively were shown to be enhanced in intensity (see Figure 7) and a vibration at 275 cm$^{-1}$, which is tentatively assigned to $\nu_s$(Mo–N).

The figure at the top shows that the maxima of the excitation profiles of all high-frequency modes have the same position, at the high frequency side of the first CT band (about 620 nm) just as for $Mo(CO)_4PyCa$.

This also holds for $\nu(CO^{cis})$ but not for the low-frequency modes which are apparently not coupled to this electronic transition.

Just as for $Mo(CO)_4PyCa$ the resonance effect is larger for $\nu$(PyII) and $\nu$(PyIII) than for $\nu$(C=N). On the other hand, the resonance effect of $\nu(CO^{cis})$ is much weaker for this compound than for $Mo(CO)_4$-PyCa. This means that orbitals of the *cis* carbonyl much less contribute to the excited state of $Mo(CO)_3$-$PyCa(PBu_3)$ than for $Mo(CO)_4PyCa$. This agrees with the stronger $\pi$-backbonding from the metal to the PyCa ligand in the first complex as shown *e.g.* by its smaller solvatochromism.

The CT band at about 450 nm is much weaker than the low-energy band and resonance effects are correspondingly much smaller as can be seen at the left side of figure 7. Furthermore, the excitation profiles are different for both bands. Although $\nu$(PyII) and $\nu$(PyIII) are both enhanced in intensity during

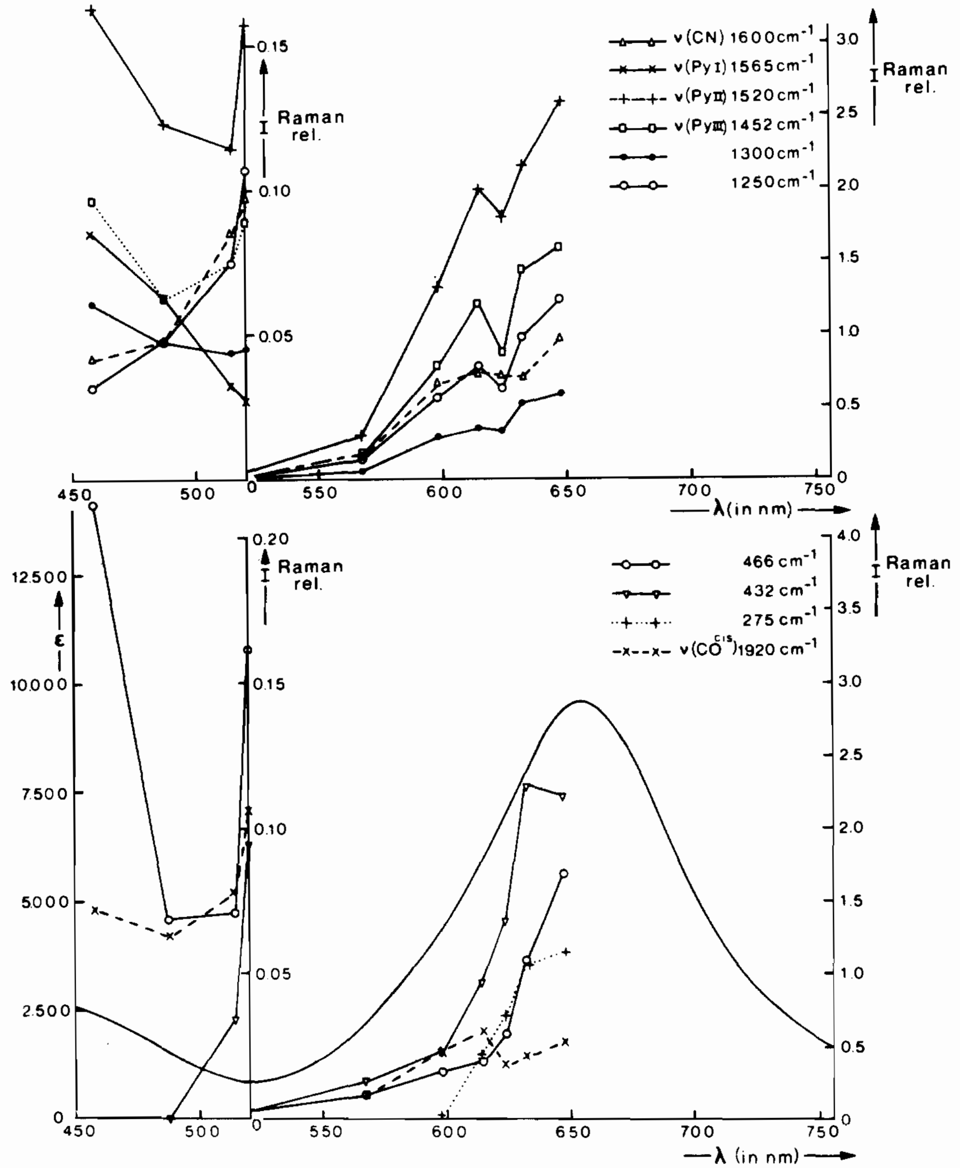


Figure 7. Excitation profiles of $Mo(CO)_3PyCa(Pbu_3)$ in $CS_2$, relative to the 397 $cm^{-1}$ band of $CS_2$.

excitation within both bands, no such effect is observed for $\nu(C{=}N)$ in the high-energy band. This means that the $a_2^*$ orbital is mainly localized at the pyridine-ring of the PyCa ligand. Resonance enhancement is observed within this band for $\nu$(PyI), which vibration does not show such an effect when excitation occurs within the long-wavelength band. The resonance effects of the two low-frequency modes at 432 and 466 $cm^{-1}$ respectively, are very remarkable. Both vibrations show resonance enhancement in the CT band [22] but only the 466 $cm^{-1}$ band is enhanced during excitation within the band at 450 nm. These vibrations must, however, properly be assigned first before conclusions can be drawn. This will be the subject of a further investigation.

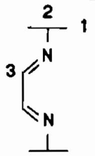
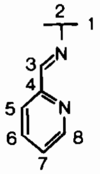
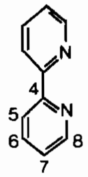
Both $Mo(CO)_4PyCa$ and $Mo(CO)_3PyCa(PBu_3)$ showed decomposition in the laser beam when excitation occurred at the high-energy side of the first CT band. This photochemical behaviour has been observed in several cases and will further be investigated.

## *NMR Spectra*

### *$^1H$ NMR spectra*

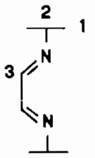
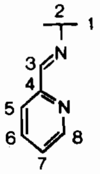
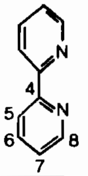
Although $^1H$ NMR does not give much information about charge densities, some typical results are presented in Table IV. For the DAB and PyCa compounds an upfield shift of $H_3$ is observed going from tetra- to dicarbonylcomplexes. These shifts are somewhat larger for the DAB-compounds. Both series of

TABLE IV. $^1$H NMR Chemical Shifts[a].

| | Ligand | Mo(CO)$_4$L | Mo(CO)$_3$L(PR$_3$) | | | | Mo(CO)$_2$L(PEt$_3$)$_2$ |
|---|---|---|---|---|---|---|---|
| | | | P(OMe$_3$) | PΦ$_3$ | PEt$_3$ | PBu$_3$ | |
|  | | | 8.12 | 7.95 | 8.10 | 8.15 | 7.60 |
| | 3 7.93 | 8.23 | | | | | 7.65 |
| | | | 8.17 | 8.00 | 8.15 | 8.21 | 7.70 |
|  | | | 8.40 | | 8.45 | 8.45 | |
| | 3 8.35 | 8.50 | | | | | 8.20 |
| | | | 8.45 | | 8.50 | 8.50 | |
| | 8 8.55 | 9.01 | 8.97 | | 9.01 | 9.05 | 8.93 |
| | 8.62 | 9.08 | 9.04 | | 9.08 | 9.12 | 9.00 |
|  | 8 8.60 | | 9.05 | | 9.10 | 9.10 | 9.02 |
| | 8.67 | | 9.12 | | 9.17 | 9.17 | 9.09 |

[a]Spectra were recorded in CDCl$_3$, in ppm relative to an internal TMS standard.

TABLE V. $^{13}$C NMR Chemical Shifts.[a]

| | Ligand | Mo(CO)$_4$L | Mo(CO)$_3$L(PR$_3$) | | | | Mo(CO)$_2$L(PEt$_3$)$_2$ |
|---|---|---|---|---|---|---|---|
| | | | P(OMe)$_3$ | PΦ$_3$ | PEt$_3$ | PBu$_3$ | |
|  | | | | 25.43 | | | |
| | 1 23.32 | 24.21 | 24.21 | 24.89 | | | |
| | | | | 24.01 | | | |
| | 2 61.13 | 66.13 | 64.50 | 62.67 | 63.70 | 63.62 | 61.89 |
| | 3 159.10 | 155.80 | 153.30 | 152.47 | 150.47 | 150.05 | 137.51 |
| | | | 153.20 | | | | |
|  | * | | 23.58 | | | | |
| | 1 23.10 | 23.98 | 24.00 | | | | |
| | | | 24.36 | | | | |
| | 2 60.30 | 65.67 | 64.89 | | 64.38 | 64.10 | |
| | 5 120.25 | 125.91 | 124.51 | | 124.05 | 123.95 | |
| | 7 123.43 | 127.28 | 126.58 | | 126.70 | 126.78 | |
| | 6 135.29 | 137.14 | 135.55 | | 134.58 | 134.68 | |
| | 8 148.38 | 152.71 | 152.38 | | 151.94 | 151.77 | |
| | 4 154.13 | 153.69 | 154.31 | | 154.23 | 154.31 | |
| | 3 158.19 | 159.54 | 157.47<br>157.31 | | 155.93<br>155.76 | 156.02 | |
|  | 5 120.58 | | 121.41 | | 121.60 | 121.76 | 123.47 |
| | 7 123.21 | | 123.95 | | 124.17 | 124.07 | 126.84 |
| | 6 136.34 | | 136.14 | | 135.49 | 135.87 | 141.47 |
| | 8 148.69 | | 151.96 | | 151.96 | 151.91 | 148.98 |
| | 4 155.72 | | 154.03 | | 152.50 | 154.08 | 151.69 |

[a]Spectra were recorded in CDCl$_3$, in ppm relative to TMS.
*Assignment according to ref. 24.

TABLE VI. $^{31}P$ NMR Chemical Shifts.

| | | Mo(CO)$_3$L(PR$_3$) | | | |
|---|---|---|---|---|---|
| | | P(OMe)$_3$ | PΦ$_3$ | PEt$_3$ | PBu$_3$ |
| Free phosphine [a] | | −141.00 | 7.0 | 20.11 | 32.72 |
| L = DAB | δ | −153.93[b] | −33.46[c] | −10.23[c] | − 3.98[c] |
| | Δ | − 12.93 | −40.46 | −30.34 | −36.70 |
| L = PyCa | δ | | | − 7.35[b] | − 0.94[c] |
| | Δ | | | −27.46 | −33.66 |

[a]Ref. 26. [b]Spectra recorded in CDCl$_3$. [c]Spectra in $C_6D_6$.
Shifts are reported in ppm with respect to 85% $H_3PO_4$. The coordination chemical shift is defined as $\Delta = \delta_{complex} - \delta_{free\ ligand}$.

complexes show the same value for the $^{31}P$–$^1H_3$ coupling constants ( $|J_{PH}|$ = 2–3 Hz) [18]. Furthermore, the pyridineprotons of the PyCa and bipy compounds show the same trends.

The methyl protons of the i-propyl groups, which are not included in the table, show the presence of a pronounced steric interaction between the i-propyl group and the phosphine ligand. Two doublets are observed between 1.00 and 2.00 ppm [10] which strongly depend on the bulkiness of the phosphine group. At room temperature two methyl signals are found for the compounds of Pϕ$_3$ ($\theta$ = 145°, $\theta$ is the cone angle) and PBu$_3$ ($\theta$ = 132°), which corresponds to an inequivalence of the methylgroups due to hindered rotation about the N–C axes [23]. Only one doublet is found for the PEt$_3$ ($\theta$ = 132°) and P(OMe)$_3$ ($\theta$ = 107°) complexes. When cooled till −45 °C a strong broadening of the methyl signal is only observed in the case of P(OMe)$_3$ complexes.

### *$^{13}C$ NMR spectra*

In the series $Mo(CO)_{4-x}DAB(PR_3)_x$ a strong shielding of the $C_3$ atom occurs with respect to the free-ligand atom (Table V), which effect is consistent with an increasing charge density in the N=C–C=N moiety.

$\pi$-Backdonation from metal to ligand plays an important role in the bonding mechanism and becomes dominant in *e.g.* $Mo(CO)_2DAB(PEt_3)_2$. Here the upfield shifts correspond to a large increase of electrondensity in the whole ligand. The $Mo(CO)_3$-$DAB(PR_3)$ series nicely reflects the influence of increasing basicity of the PR$_3$ group on the Mo–L moiety and these results agree well with the trends observed for the $\nu$(CO) frequencies, as discussed before. The steric properties of the PR$_3$ ligands are determined by their cone angles and by the bulkiness of the R group [15, 16], which latter effect is demonstrated by comparing the $^{13}C$ and $^1H$ NMR spectra of $Mo(CO)_3L(PEt_3)$ and $Mo(CO)_3L(PBu_3)$ ($\theta_{PEt_3} \sim \theta_{PBu_3}$; basicity of PEt$_3$ $\lesssim$ that of PBu$_3$). In the case of the PΦ$_3$ complex hindered rotation about the N–C axes is observed, just as found in the $^1H$ NMR spectra [23].

In the series $Mo(CO)_3PyCa(PR_3)$ the upfield shifts of $C_3$ are much smaller than in the DAB complexes, and large downfield shifts are observed for $C_5$, $C_7$, $C_8$ and $C_2$. These shifts are larger in the pyridine ring than in the C=N–(i-propyl) group. As a result charge-shifts will be larger in the $N^{py}$–Mo–$CO_1^{trans}$ direction than in the $N^{C=N}$–Mo–$CO_2^{trans}$ direction, which is consistent with the presence of two different $CO^{trans}$ signals observed for $Mo(CO)_4PyCa$ at 222.83 ppm and 223.38 ppm respectively. This asymmetric coordinative behaviour of the PyCa ligand also appeared from the resonance Raman spectra.

In all complexes the charge density in the PyCa ligand decreases with respect to the free molecule, indicating a dominant $\sigma$-bonding mechanism. $\sigma$-bonding in the PyCa complexes seems to be stronger than in the DAB complexes, because the observed $^{31}P$–$^{13}C_3$ coupling constants are larger in PyCa complexes ( $|J_{PC}|$ = 3.2–3.5 Hz) than in DAB complexes ( $|J_{PC}|$ = 2.0 Hz) [25]. This conclusion agrees with the larger downfield shifts of $C_2$ for all complexes and $C_3$ for $Mo(CO)_4PyCa$, with respect to the free ligand shifts.

In the bipy complexes the charge density in the N=C–C=N moiety increases, just as for the DAB and PyCa complexes. The charge density in the whole ligand however, decreases, just as for PyCa complexes. $\sigma$-donation from ligand to metal is of main importance in the bonding mechanism of bipy complexes, while $\pi$-backbonding is relatively weak, as also appeared from IR and UV results.

The difference between $Mo(CO)_3bipy(PEt_3)$ and $Mo(CO)_3bipy(PBu_3)$ can hardly be explained as a result of steric interaction, because bipy is very small compared with DAB and PyCa.

### *$^{31}P$ NMR spectra*

Little is known about the interpretation of the absolute values of the coordination shifts ($\Delta$). The sign of these shifts is evident when it is assumed that the formation of a σ-donor bond from phosphorus to molybdenum results in a decrease of electron density on the phosphorus atom with a decrease in the shielding and in the δ value. Mann *et al.* showed that a linear relation exists between the $^{31}P$ chemical shift of the free tertiary phosphine ($\delta_{free}$) and the change in $^{31}P$ chemical shift on coordination (Δ), *i.e.* $\Delta = A + B\delta_{free}$ [26–28]. However, this empirical relationship appeared to hold only in the case where no large steric effects are present [28], because the $^{31}P$ chemical shifts appear to be very sensitive for these steric interactions [29]. This empirical relationship holds for our complexes with the exception of $Mo(CO)_3DAB(P\Phi_3)$. The large Δ observed for this latter compound may result from the strong steric interaction, between $P\Phi_3$ and the isopropyl group as has been deduced from the $^1H$ and $^{13}C$ NMR results. Furthermore, the phosphine groups in the DAB complexes are more sterically hindered than in the PyCa complexes, which effect may explain the smaller coordination shifts of the PyCa compounds with respect to the DAB complexes.

## Conclusions

All spectroscopic results clearly indicate that the coordinate behaviour of PyCa is much more determined by the pyridine ring than by the C=N group. In this respect the ligand much more resembles bipy than DAB.

The resonance Raman effect gave valuable information about the characters of the electronic transitions and the properties of the excited states of these complexes [20, 30].

It has been shown that CT transitions from the metal to the second excited state of the bidentate ligand can be visualised and assigned by substitution of CO by $PR_3$.

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