The Chemical Oxidation and Electronic Spectra of the Complexes

trans-[M(CNR)$_2$(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$] (M = Mo or W)

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Summary

Oxidation of the complexes trans-[M(CNR)$_2$(dppe)$_2$] (A)
(M = Mo or W; R = Me, Bu^t or CH$_3$C$_6$H$_4$-4; dppe = Ph$_2$P-
CH$_2$CH$_2$PPh$_2$) with diiodine or silver (I) salts gives
the paramagnetic cations trans-[M(CNR)$_2$(dppe)$_2$]$^+$, (M = Mo,
R = CH$_3$C$_6$H$_4$-4; M = W, R = Bu^t) and trans-[M(CNR)$_2$(dppe)$_2$]$^{2+}$
(M = Mo, R = Me or CH$_3$C$_6$H$_4$-4; M = W, R = Me or Bu^t).
Mixtures of products are generally produced when
dichlorine or dibromine are the oxidising agents,
however pure salts , the seven-coordinate complex
cations [MX(CNC$_6$H$_4$CH$_3$-4)$_2$(dppe)$_2$]$^+$ (B, X = Cl or Br)
have been isolated. A simple molecular orbital scheme
is proposed for complexes (A) and used to discuss
their electronic spectra and their oxidation.

We have recently described the preparation of the complexes
trans-[M(CNR)$_2$(dppe)$_2$] (A) in which the strong electron –
releasing nature of the electron-rich metal causes a large
lowering of the CN stretching frequencies and a non-linear
CNMe angle [156(1)°] in (A, M = Mo, R = Me).[1,2] Complexes (A)

can be electrochemically oxidised reversibly by one unit and irreversibly by two units.[2] These observations prompted us to examine their chemical oxidation. Depending upon the reaction conditions and of the nature of the starting complex (A), we have isolated mono- or di-cationic, six- or seven-coordinate complexes from these oxidation reactions. We have also measured the electronic spectra of complexes (A) and relate these data and the chemical and electrochemical oxidations to a simple molecular orbital scheme for (A).

Chemical Oxidations

The oxidation reactions of complexes (A) generally tended to be complicated, leading to a mixture of products in various oxidation states. The number of complexes which could be isolated was therefore limited and strongly dependent upon reaction conditions. Nevertheless, three types of cationic complexes were prepared and are shown in Table 1 together with details of their characterisation.

The mono-cations $[M(CNR)_2(dppe)_2]^+$ (M = Mo, R = $CH_3C_6H_4-\underline{4}$; M = W, R = Bu^t) were prepared by the iodine oxidation in benzene at 20° of the appropriate (A) complexes [reaction (1)].

$$[M(CNR)_2(dppe)_2] + \tfrac{1}{2}I_2 \longrightarrow [M(CNR)_2(dppe)_2]I$$
$$\downarrow NaBPh_4$$
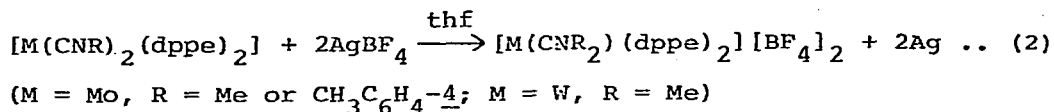$$[M(CNR)_2(dppe)_2]BPh_4 \qquad \cdots (1)$$
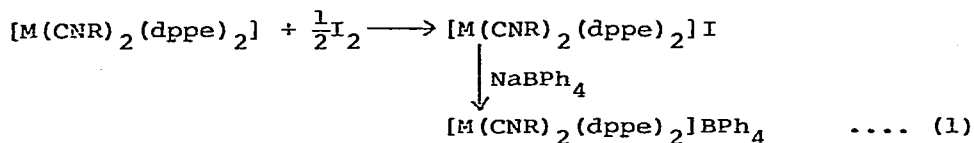
In one case (M = Mo, R = $CH_3C_6H_4-\underline{4}$) the iodide anion was exchanged for BPh_4. Monocationic complexes were obtained by an analogous reaction to (1) using silver (I) as oxidising agent [Ag(I):M atom = 1:1) but dicationic complexes were obtained by use of a ratio 2Ag(I):M atom as in equation (2). Both series appear to have <u>trans</u>-configurations [only one $\nu(NC)$ value (Table 1)]

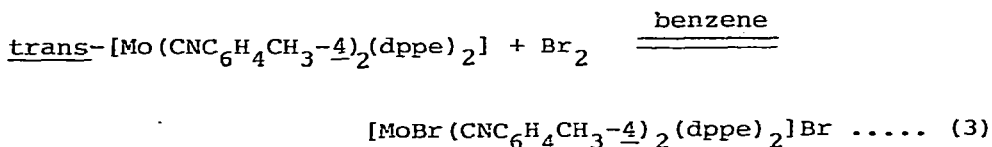TABLE 1.   Isonitrile complexes of molybdenum and tungsten

Complex[a]	Yield	Colour	Mp[b]	Analysis[c] C	H	N	ν(NC)[d]	Λ_m	μ_eff
[W(CNBu^t)_2(dppe)_2]I.½C_6H_6	39	yellow	208-209 dec	59.5(59.5)	5.4(5.3)	2.2(2.1)	2000	98[e]	1.77
[Mo(CNC_6H_4CH_3)_2(dppe)_2]BPh_4.½CH_2Cl_2	37	yellow	230-232	74.8(74.6)	5.4(5.6)	1.7(1.9)	1956	61[f]	2.01
[Mo(CNC_6H_4CH_3)_2(dppe)_2]BF_4	42	yellow	267-271	67.4(67.3)	5.3(5.2)	2.3(2.3)	1953	75[f]	1.91
[W(CNMe)_2(dppe)_2](BF_4)_2	65	pink	179-181	54.8(54.4)	4.7(4.7)	2.4(2.3)	2108	134[e]	2.45
[W(CNBu^t)_2(dppe)_2]Cl_2.C_6H_6 [g]	64	yellow-pink	185 dec	62.7(63.0)	5.8(5.6)	2.3(2.2)	2019	123[f]	2.65
[Mo(CNMe)_2(dppe)_2](BF_4)_2	40	cerise	185-192 dec	58.2(58.6)	4.8(4.7)	2.3(2.4)	2127	133[f]	3.06
[Mo(CNC_6H_4CH_3)_2(dppe)_2](BF_4)_2	51	brown	148-149	62.8(62.8)	4.9(4.0)	2.2(2.2)	2052	165[f]	2.55
[MoCl(CNC_6H_4CH_3)_2(dppe)_2]BPh_4 [h]	58	orange	215 dec	74.3(74.6)	5.9(5.6)	2.0(1.9)	1980	52[i]	dia
[MoBr(CNC_6H_4CH_3)_2(dppe)_2]Br	45	yellow	106 dec	63.2(63.5)	5.2(4.9)	2.2(2.2)	1950	23[j]	dia

a for probable configurations see text.   b in sealed evacuated tubes.   c calculated values in parentheses.   d nujol mulls
e approx 10^{-3} PhNO_2 solution.   f approx 10^{-3} Me_2NCHO solution.   g Cl analysis 5.7(5.5).   h Cl analysis 2.9(2.4); ν(MoCl) = 385 cm^{-1}.   i approx 10^{-3} MeNO_2 solution.   j approx 10^{-3} C_2H_2Cl_2 solution, but decreasing with time.   dia = diamagnetic

$$[M(CNR)_2(dppe)_2] + 2AgBF_4 \xrightarrow{\text{thf}} [M(CNR_2)(dppe)_2][BF_4]_2 + 2Ag \quad .. \quad (2)$$

(M = Mo, R = Me or $CH_3C_6H_4-\underline{4}$; M = W, R = Me)

An alternative route to the dicationic complexes, successful for the complex $[W(CNBu^t)_2(dppe)_2]Cl_2$, was careful addition of exactly one mole of dichlorine to (A, M = W, R = Bu^t) in benzene. Magnetic data for these paramagnetic mono- and di-cationic complexes are in Table 1.

Further reaction, involving addition of halide at the metal, occurred when dichlorine or dibromine were used as the oxidising agents, so that the isolation of products was difficult. Two molybdenum halide complexes were isolated from such reactions, they are the seven-coordinate cations $[MoX(CNC_6H_4CH_3-\underline{4})_2(dppe)_2]^+$ (B, X = Cl or Br) prepared by oxidation of (A, M = Mo, R = $CNC_6H_4CH_3-\underline{4}$; M = W, R = Me) with dibromine e.g. (equation (3)) or by an excess of $FeCl_3$ in ethanol, followed by anion exchange with $NaBPh_4$ (See experimental). The observation of an Mo-Cl stretching band in the i.r. spectrum of the chloride complex (Table 1) shows that the inner-sphere halide ligates the metal.

$$\underline{trans}\text{-}[Mo(CNC_6H_4CH_3-\underline{4})_2(dppe)_2] + Br_2 \xrightarrow{\text{benzene}}$$

$$[MoBr(CNC_6H_4CH_3-\underline{4})_2(dppe)_2]Br \quad ..... \quad (3)$$

Complexes (B) are diamagnetic and their n.m.r. spectral data are shown in Table 2.

Reversible one electron and irreversible 2 electron oxidation of complexes (A) was observed electrochemically in the presence of lithium halides.[2] It is probable that the irreversibility of the two-electron oxidation was due to the

TABLE 2. ^{1}H n.m.r. spectra[a] of seven-coordinate complexes

Complex	δ ppm ($\pm$ 0.01)	Integration[b]	Assignment
$[MoCl(CNC_6H_4CH_3\text{-}\underline{4})_2(dppe)_2]BPh_4$	7.8-6.7m	64(64)	$B(C_6\underline{H}_5)_4$ + dppe, aromatic-$\underline{H}$ $CNC_6\underline{H}_4CH_3$, ortho to CH_3
	5.94d[c]	4(4)	$CNC_6\underline{H}_4CH_3$, ortho to N
	2.9-2.1m, br	8(8)	$C\underline{H}_2$ of dppe
	2.24s	6(6)	$CNC_6H_4C\underline{H}_3$
$[MoBr(CNC_6H_4CH_3\text{-}\underline{4})_2(dppe)_2]Br$	8.0-6.4m	44(44)	dppe, aromatic-$\underline{H}$ + $CNC_6\underline{H}_4CH_3$, ortho to CH_3
	6.3-6.0m	4(4)	$CNC_6\underline{H}_4CH_3$, ortho to N
	2.9-2.0m, br	7(8)	$C\underline{H}_2$ of dppe
	1.83s	5(6)	$CNC_6H_4C\underline{H}_3$

[a] in CD_2Cl_2 relative to $SiMe_4$. [b] calculated values in parentheses

[c] $^3J(HH) = 8.0 \pm 0.5$ Hz

m = multiplet, s = singlet, br = broad.

addition of halide ion at the metal (II) centre in those
experiments, as has been observed here when dichlorine or
dibromine are the oxidising agents. As expected from the
electrochemical oxidations, the mono-cationic six-coordinate
complexes are reduced back to their precursors (A) by lithium
in thf. In the same solvent, the six-coordinate dicationic

complexes can also be reduced to their mono-cationic analogues by magnesium. No characterisable product was obtained on attempted reduction of the seven-coordinate complexes.

i.r. and n.m.r. spectra

As expected, the oxidised complexes show values in their i.r. spectra of $\nu(NC)$ which are increased by about 200-300 cm^{-1} relative to their precursor complexes (A).[2] The six-coordinate dications show the greatest relative increase of $\nu(NC)$ with the values of the seven-coordinated complexes lying between these values and those of the six-coordinate mono-cations. Evidently the seven-coordinate complexes, despite their formal M(II) oxidation state, have a lower effective oxidation state than their six-coordinate dicationic analogues because of the release of negative charge to the metal atom from the halide ion.

It is notable that the two seven-coordinate complexes (B) clearly have different structures since their i.r. spectroscopic properties differ (Table 1). The complex [MoCl(CNC$_6$H$_4$-Me-4)$_2$(dppe)$_2$]BPh$_4$ may have a similar structure (capped trigonal prismatic) to its analogue [WI(CO)$_2$(Me$_2$PCH$_2$CH$_2$PMe$_2$)$_2$]I[3] in keeping with its two $\nu(NC)$ values, but [MoBr(CNC$_6$H$_4$Me-4)$_2$-(dppe)$_2$]Br has only one $\nu(NC)$ value and its structure could be similar either to that of [WH(N$_2$)$_2$(dppe)$_2$]HCl$_2$ (pentagonal pyramidal)[4] which has apical dinitrogen ligands and a single N_2 i.r. band or to those of [MH(XY)(dppe)$_2$]$^+$ (M = Mo or W, XY = CO[5] or RNC[6]) which are most probably face capped octahedral, but only show a single i.r. (XY) band.

In the ^{1}H n.m.r. spectrum of [MoCl(C$_6$H$_4$Me-4)$_2$(dppe)$_2$]BPh$_4$ a doublet is observed at $\delta = 5.94$ which appears to be the high field half of an AB spectrum which arises from the phenyl protons. The lower field half is obscured by the phenyl (dppe) complex multiplet. The high field half may be assigned to the

phenyl ring protons in <u>ortho</u>-positions relative to the N atoms by analogy with the spectrum observed for $[Co(CNC_6H_4NO_2-\underline{4})_2-\{PPh(OEt)_2\}_3]ClO_4$.[7] The coupling constant $^3J(H_A-H_B)$ for the molybdenum complex (8.0 Hz) is similar to that reported for the cobalt complex (9 Hz).[7] The ^1H n.m.r. spectrum of $[MoBr(CNC_6-H_4CH_3-\underline{4})_2(dppe)_2]Br$ exhibits an unresolved complex multiplet at δ 6.3–6.0, which may be due to the high field half of an AA'BB'-type pattern of the phenyl protons. The magnetic inequivalence of the four protons of the phenyl ring of each isonitrile is conceivable in a seven-coordinate complex.

Electronic Spectra

Complexes (A) show, in general, two main absorptions (Table 3) with the lower energy band also of a lower relative intensity. For (A, R = aromatic) there are some additional absorptions, relative to (A, R = alkyl), which are broad, in the range 260–270 nm and 310–320 nm, and probably originate in the aromatic rings.

Of the main absorptions, we assign the lower frequency band, the energy of which is dependent upon the group R, (Table 3) to a metal $\longrightarrow$ isonitrile charge-transfer transition. Similar assignments have been made for related isonitrile complexes, for example in the series $[M(RNC)_y(CO)_{6-y}]$ ($y = 1$, $M = Cr$;[8] $x = 2$ or 3, $M = Cr$ or Mo;[8] $y = 6$, $M = Cr$, Mo or W[9].). For (A, R = aromatic) the energy of this transition is lower than for (A, R = aliphatic). We also find that the energy of this band (as measured by $\frac{1}{\lambda_1}$ values), the $E_{\frac{1}{2}}$ values of the complexes (A, R = aromatic), and the values of σ_p for the <u>para</u>-substituent of R in (A, R = aromatic) have a similar dependence upon R. Thus a linear correlation of $\frac{1}{\lambda_1}$ occurs with $E_{\frac{1}{2}}$ values and with σ_p values (Fig. 1). The values for

TABLE 3. Electronic spectra of trans-[M(CNR)$_2$(dppe)$_2$] in thf (260-850 nm)[a]

|	R	λ_1 (log ε_1)	λ_2 (log ε_2)	$1/\lambda_1$	$1/\lambda_2$
M = Mo	ClC$_6$H$_4$-4	485(3.51)	350(4.06)	2062	2865
	Ph	481(3.82)	389(4.31)	2081	2558
	CH$_3$C$_6$H$_4$-4	473(4.05)	390(4.49)	2114	2564
	CH$_3$OC$_6$H$_4$-4	463(3.98)	377(4.46)	2160	2653
	Me	385(4.08)	291(4.35)	2597	3436
	Bu^t	391(3.86)	293(4.29)	2557	3413
M = W	ClC$_6$H$_4$-4	487(3.55)	364(4.14)	2054	2755
	Ph	478(3.86)	374(4.44)	2092	2674
	CH$_3$C$_6$H$_4$-4	474(4.08)	379(4.56)	2112	2632
	CH$_3$OC$_6$H$_4$-4	463(3.99)	369(4.49)	2160	2710
	Me	381(4.13)	286(4.41)	2625	3497
	Bu^t	387(4.02)	288(4.45)	2587	3472

[a] λ values in nm $\pm$ 1 nm; $1/\lambda$ values in cm^{-1} $\pm$ 5 x 10^{-1}

(A) of the fractional lowering of ν(NC) on coordination ($\frac{\Delta\nu}{\nu}$) also show a dependence which is related to $\frac{1}{\lambda_1}$ values but is not linear.

Discussion

The π-molecular orbital scheme for complexes (A) shown in Fig. 2, although an over simplifications, nevertheless allows a reasonable qualitative discussion of the above correlations and of the properties of the oxidised complexes. The scheme, which resembles that used to discuss[10] the bonding in trans-[M(N$_2$)$_2$(dppe)$_2$] [the precursor to (A)][2] is constructed from the metal d-orbitals and the C- and N- p-orbitals. This
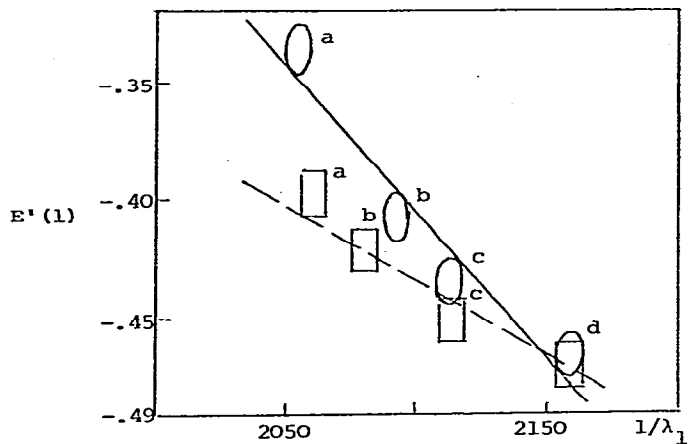
i)   M = W(O); M = Mo (☐)
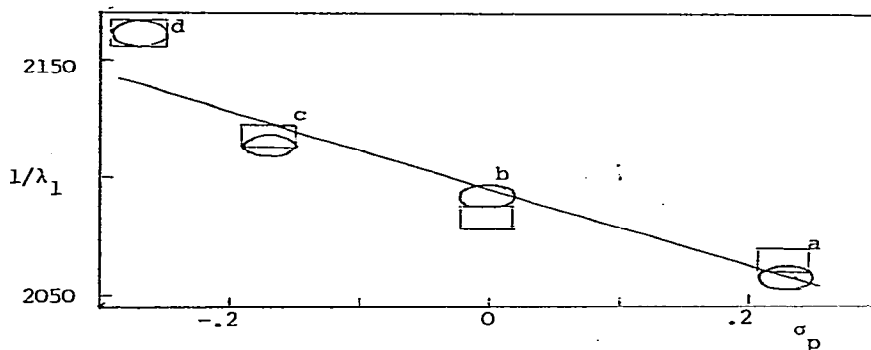
ii)   M = W(O); M = Mo(☐)

FIG.1.   Dependence of $\frac{1}{\lambda_1}$ upon   i) E'(1)[e] and ii) σ_p[f]

values for trans-$[M(CNC_6H_4Y-4)_2(dppe)_2]$[g]

[e] E'(1) = $\frac{1}{2}[Ep_a(1) + Ep_c(1)]$, see ref 2 for details.   [f] σ_p values taken

from R.W. Taft, J. Phys. Chem., 1960, 64, 1805.   [g] Y = Cl(a), H(b),

CH_3(c), CH_3O(d).

gives, for a linear system [Fig. 2(a)] a set of degenerate

levels (in idealised D_{4h} symmetry) and a non-bonding metal

d-orbital (b_{2g}).   It has been shown that trans-$[Mo(CNMe)_2(dppe)_2]$

has a non-linear CNMe group (angle CNMe = 156°)[1] and this

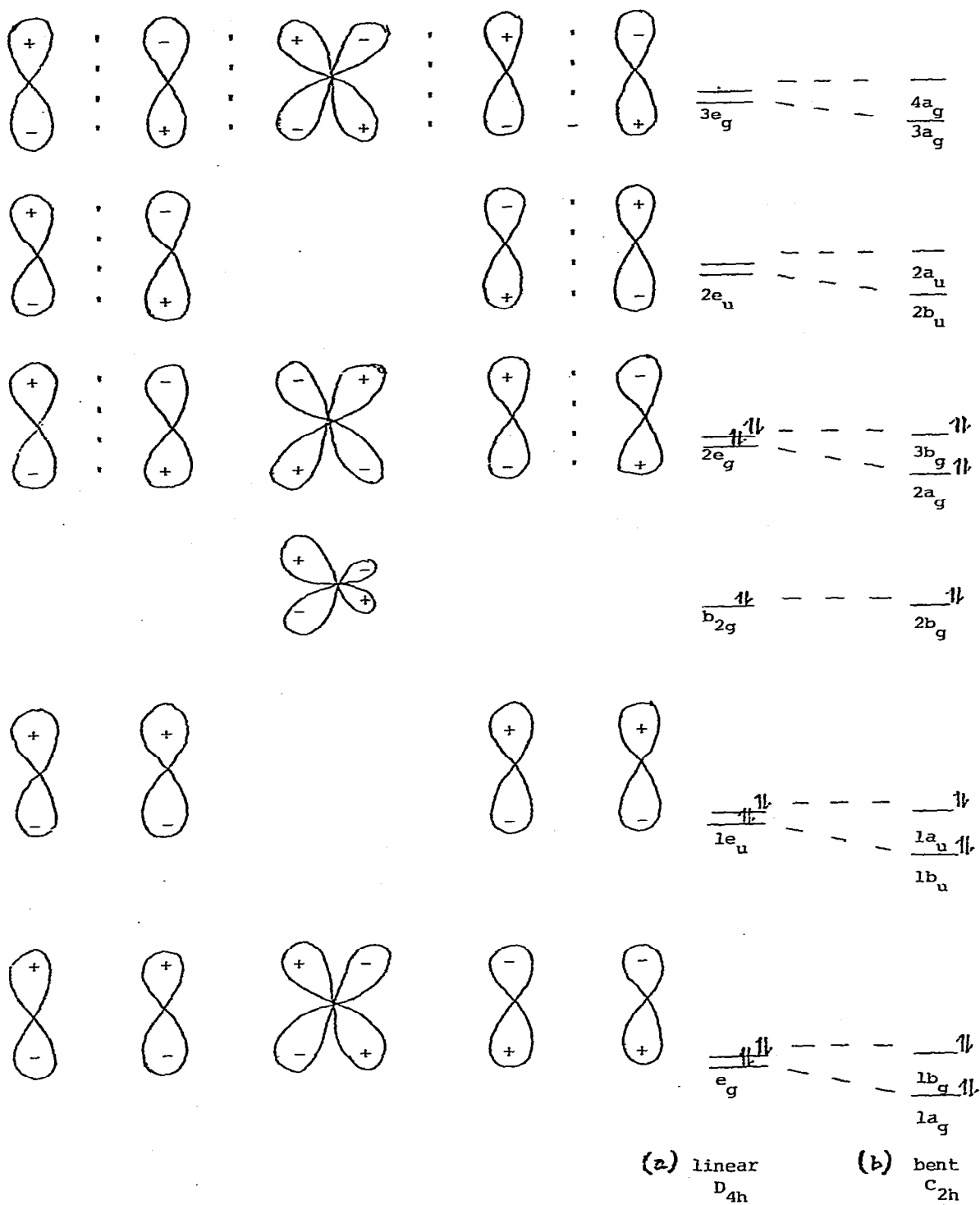deviation from linearity is accommodated in Fig. 2(b), following

FIG. 2.

Simplified M.O. scheme for (R)NCMCN(R) system

the arguments of Walsh and of Gimarc[11] by removing the degeneracy
of the e-levels of Fig. 2(a) by interaction of a carbon hybrid
σ-orbital with the nitrogen p-orbitals in one plane. Thus a
new set of singly-degenerate orbitals which lie at some energy
lower than the parent e-levels and a singly degenerate set at
essentially the same energy as the parent levels, result. Thus
bending causes a stabilisation of the π-levels as it proceeds
to the limit of 120°, with a concomitant destabilisation of
the σ-levels.[11] In complex (A) there appears to be a
balance at the partially bent stage but in $[Ru(CNBu^t)_4(PPh_3)]$,
full bending ($CNBu^t$ angle 120°) of a terminal isonitrile ligand
occurs[12] and π-stabilisation dominates.

The molecular orbitals of Fig. 2(b) are filled up to and
including $3b_g$. When we consider the use of Fig. 2(b) to discuss
the properties of complexes (A) a problem arises because the
relative ordering of the $3b_g$ and $2b_g$ levels is not known.
However, as is shown, we favour $3b_g$ as the higher occupied
level as apposed to $2b_g$, because this assignment appears to fit
most reasonably the properties of complexes (A) as discussed
below.

Removal of electrons from $3b_g$, since it has C-N anti-
bonding character, would be expected to increase the C-N bond
order and therefore $\nu(CN)$. An increase in $\nu(CN)$ is observed
in the oxidised species reported above. A correlation would
also be expected between $E_{\frac{1}{2}}$ for removal of an electron from
$3b_g$ in (A, R = aromatic) and σ_p for substituents on the
aromatic ring, since $3b_g$ contains contributions from the CN
and the R orbitals, whereas such a correlation, although
possible, is less convincing if $2b_g$ were the redox orbital.

Promotion of an electron from $2b_g$ (or $2a_g$ or $2b_g$) to $2b_u$
(the lowest unoccupied level) is equivalent to charge transfer

from the metal to the isonitrile π^* levels and gives rise to the observed electronic spectrum. The linear correlation between $E_{\frac{1}{2}}$ and $\frac{1}{\lambda_1}$ values (Fig. 1) suggest that the redox orbital and the highest occupied molecular orbital are the same and therefore most likely $3b_g$. The observed lower energy of the charge transfer transition for (A, R = aromatic) described above, may arise because of an additional stabilisation of the π^*-orbitals (from $2e_u$ in D_{4h} symmetry) due to their bonding interaction with π^* orbitals on the phenyl ring.[9,13] Presumably this stabilisation is greater for $2e_u$ (and for $2a_u$ and $2b_u$) than for the highest occupied molecular orbital (assumed $2e_g$ derived orbitals) although $E_{\frac{1}{2}}$ measurements show that this level is also stabilised relative to (A, R = alkyl). Thus as electron withdrawing groups are substituted onto the phenyl ring the charge-transfer band energy decreases, as $2e_u$ is stabilised, but $E_{\frac{1}{2}}$ increases as the highest occupied molecular orbital is stabilised. This results in the linear inverse relationship shown in Fig. 1. A similar relationship was also observed for the complexes $[Co(PPh_3)_2(CNR)_3]^+$ (R = C_6H_5, $C_6H_4CH_3-\underline{4}$ or $C_6H_4Cl-\underline{4}$)[14] but for $[Fe(1,\underline{10}-phenanthroline)_2(CNBX_3)_2]$ (X = Me, H, F, Cl or Br) a $\underline{direct}$ linear correlation between $E_{\frac{1}{2}}$ (oxidation) and (metal $\longrightarrow$ ligand) charge-transfer transitions is observed as X varies.[15] Presumably the former case is similar to (A) above but in the iron complexes, the lowest unoccupied molecular orbital presumably is essentially phenanthroline-π^* in character and will be unaffected by variation of X, whereas the highest occupied molecular orbital (redox orbital) and thus the values of $E_{\frac{1}{2}}$ and the charge-transfer transition energy, will vary directly with X. As would be expected from the above discussion there is a linear dependence between $\frac{1}{\lambda_1}$ and σ_p for the phenyl ring substituents in (A, R = aromatic) (Fig. 1).

The energy separation between the highest occupied and lowest unoccupied molecular orbitals for (A, R = alkyl) appears to be similar to the corresponding energy in the parent bis(dinitrogen) complexes trans-$[M(N_2)_2(dppe)_2]$ (M = Mo or W) since the charge–transfer transitions have about the same energy for both series [circa 381–399 nm for (A, R = alkyl); circa 380 nm for the dinitrogen complexes]. A somewhat lower transition energy is observed for (A, R = aromatic) as described earlier.

For (A, R = alkyl) both the $\frac{1}{\lambda_1}$ and $E_{\frac{1}{2}}$ values increase on passing from R = Bu^t to R = Me but the limited number of data and tendency for anomolous behaviour of Bu^t substituted complexes[2] do not allow a rationalisation of this behaviour.

Thus the behaviour of these low valent isonitrile complexes can be rationalised reasonably well using a very simplified M.O. scheme. More quantitative assessment or prediction of the degree of bending at the isonitrile nitrogen must, however, await the development of more sophisticated schemes based upon calculation, of the type under development for M–N–N–H and related complexes.[16]

Experimental

All air–sensitive materials were handled using standard nitrogen–flow or high–vacuum techniques. The complexes trans-$[M(CNR)_2(dppe)_2]$ were prepared by published methods.[2] All other reagents were analytical grade and were used without further purification. Tetrahydrofuran (thf) was distilled from sodium benzophenone ketyl before use and all other solvents were dried and distilled under dinitrogen prior to use. Infra-red spectra were determined with a Unicam SP 200 or Perkin Elmer 577 Instruments and n.m.r. spectra with a JEOL PS 100 or Varian EM 360 spectrometers. Conductivities were measured using a

Portland Electronics P310 conductivity bridge and melting points
with an Electrothermal Melting Point Apparatus. Magnetic
susceptibilities were determined with a Faraday Balance.
Microanalyses were by Mr & Mrs Olney of the University of Sussex.

Preparation of Oxidised Species

Bis[bis(diphenylphosphino)ethane]bis(tertiarybutylisonitrile)
tungsten(I) (Iodide). [W(CNBu^t)$_2$(dppe)$_2$]I. – trans-[W(CNBu^t)$_2$-
(dppe)$_2$] (0.120 g, 0.105 mmole) was dissolved in benzene (15 cm^3)
and iodine (0.0463 mmole) in benzene (0.72 cm^3) was slowly added
dropwise. During this addition the colour of this solution
changed from red to yellow and yellow microprisms of the
product slowly appeared, which were filtered, washed with
benzene and dried in a vacuum (20°, 10^{-3}mm)(0.048 g, 39%). The
product contained benzene of crystallisation.

Bis[bis(diphenylphosphino)ethane]bis(para-tolylisonitrile)
molybdenum(I) Tetraphenylborate, [Mo(CNC$_6$H$_4$CH$_3$-4)(dppe)$_2$]BPh$_4$. –
To a benzene solution (20 cm^3) of trans-[Mo(CNC$_6$H$_4$CH$_3$-4)$_2$(dppe)$_2$]
(0.140 g, 0.124 mmole) was added iodine (0.062 mmole) in benzene
(1 cm^3) slowly dropwise. A yellow suspension formed which was
filtered and the resulting solid washed with benzene and dried.
It was then dissolved in thf (10 cm^3) and NaBPh$_4$ (0.14 g) was
added. The resulting solution was then taken to dryness and
the resulting solid was extracted with dichloromethane to give
a red solution which after filtration and concentration gave
yellow crystals of [Mo(CNC$_6$H$_4$CH$_3$-4)$_2$(dppe)$_2$]BPh$_4$ (0.07 g,
0.046 mmole, 37%). The product contained dichloromethane
of crystallisation.

Bis[bis(diphenylphosphino)ethane]bis(para-tolylisonitrile) molybdenum(I) Tetrafluroborate, [Mo(CNC$_6$H$_4$CH$_3$-4)$_2$(dppe)$_2$]BF$_4$. – A solution of AgBF$_4$ (0.104 mmole) in thf (1.68 cm^3) was added dropwise to trans-[Mo(CNC$_6$H$_4$CH$_3$-4)$_2$(dppe)$_2$] (0.117 g, 0.104 mmole) in thf (30 cm^3). A fine black precipitate of silver metal rapidly formed and the mixture was filtered. The resulting red solution was concentrated in a vacuum and yellow crystals of the product precipitated (0.053 g, 0.044 mmole, 42%).

Bis[bis(diphenylphosphino)ethane]bis(methylisonitrile)tungsten(II) Bistetrafluroborate, [W(MeNC)$_2$(dppe)$_2$](BF$_4$)$_2$. – AgBF$_4$ (0.31 mmole) in thf (2.5 cm^3) was added dropwise to a red solution of trans-[W(MeNC)$_2$(dppe)$_2$] (0.162 g, 0.153 mmole) in thf (35 cm^3). The resulting yellowish-brown solution was separated from the precipitated silver by filtration. Concentration in a vacuum of the resulting solution followed by addition of ether gave an oil which solidified after freezing with liquid nitrogen, warming to 20° and stirring for 16 hours. It was recrystallised from CH$_2$Cl$_2$/Et$_2$O as pink crystals (0.123 g, 0.099 mmole, 65%).

Bis[bis(diphenylphosphino)ethane]bis(tertiarybutylisonitrile) tungsten(II) Dichloride, [W(Bu^{t}NC)$_2$(dppe)$_2$]Cl$_2$. – trans-[W(CNBu^t)$_2$(dppe)$_2$] (0.12 g, 0.11 mmole) was dissolved in benzene (10 cm^3) and a freshly prepared solution of chlorine in benzene (0.08 cm^3, 0.105 mmole Cl$_2$) was slowly added. A light green suspension of the product [W(CNBu^t)$_2$(dppe)$_2$]Cl$_2$ precipitated and was filtered, washed with ether and dried (20°, 10^{-3}mm) (0.09 g, 0.07 mmole, 65%).

Bis[bis(diphenylphosphino)ethane]bis(methylisonitrile)

molybdenum(II) Bistetrafluroborate, [Mo(MeNC)$_2$(dppe)$_2$](BF$_4$)$_2$. –
To a red solution of trans-[Mo(MeNC)$_2$(dppe)$_2$] (0.15 g, 0.16
mmole) in thf (30 cm^3) was added a solution of AgBF$_4$ (0.31
mmole) in thf (3.2 cm^3) dropwise. A fine black suspension of
silver metal rapidly formed which was filtered and the resulting
brown solution was concentrated in a vacuum and stored at 4°
for 16 hours to give cerise crystals of [Mo(MeNC)$_2$(dppe)$_2$]-
(BF$_4$)$_2$ which were filtered, washed with ether and dried (20°,
10^{-3}mm)(0.071 g, 0.062 mmole, 40%).

Bis[bis(diphenylphosphino)ethane]bis(para-tolylisonitrile)

molybdenum(II) Bistetrafluroborate, [Mo(CNC$_6$H$_4$CH$_3$-4)$_2$(dppe)$_2$]-
(BF$_4$)$_2$. – An excess of AgBF$_4$ (0.57 mmole) in thf (4.3 cm^3)
was added to a solution of trans-[Mo(CNC$_6$H$_4$CH$_3$-4)$_2$(dppe)$_2$]
(0.16 g, 0.14 mmole) in thf (50 cm^3) dropwise to give an
immediate black precipitate of metallic silver. The mixture
was filtered and the resulting brown solution gave a brown oil
on addition of ether which after preliminary freezing with
liquid nitrogen and warming gave a brown solid on stirring.
This was filtered and re-crystallised from CH$_2$Cl$_2$/Et$_2$O to give
brown crystals of the oxidised complex [Mo(CNC$_6$H$_4$-4)$_2$(dppe)$_2$]
(BF$_4$)$_2$ (0.094 g, 0.073 mmole, 51%).

Bromobis[bis(diphenylphosphino)ethane]bis(p-tolylisonitrile)

molybdenum(I) Bromide, [MoBr(CNC$_6$H$_4$CH$_3$-4)$_2$(dppe)$_2$]Br. –
Dibromine (0.18 mmole) in benzene (2.8 cm^3) was added dropwise
to a solution of trans-[Mo(CNC$_6$H$_4$CH$_3$-4)$_2$(dppe)$_2$](0.20 g, 0.18
mmole) in benzene (30 cm^3). The yellow crystalline product
precipitated immediately and was filtered, washed with ether
and dried (20°, 10^{-3} mm) (45%).

Bis[bis(diphenylphosphino)ethane]chlorobis(p-tolylisonitrile)

molybdenum(I) Tetraphenylborate, $[MoCl(CNC_6H_4CH_3-4)_2(dppe)_2]BPh_4$.-

A solution of $FeCl_3$ (0.25 g) in ethanol (4 cm^3) was added drop-

wise to a suspension of trans-$[Mo(CNC_6H_4CH_3-4)_2(dppe)_2]$ (0.25 g)

in ethanol (30 cm^3). A brown solution was initially formed

followed by a yellow precipitate which was filtered and washed

with ethanol. After drying under vacuum, it was dissolved in

thf (40 cm^3) to give a brown solution to which an excess of

$NaBPh_4$ (0.2 g) was added. The colour of the solution changed

to red whereupon it was taken to dryness then extracted with

dichloromethane (20 cm^3) and the resulting brown-orange

solution was filtered and concentrated under vacuum. Hexane

(3 cm^3) was then added to give orange crystals of $[MoCl(CNC_6-$

$H_4CH_3-4)_2(dppe)_2]BPh_4$ on storage of the solution at 0° for 16 h.

A further crop of orange crystals was obtained from the mother

liquor (total yield 58%).

Reduction of Mo(II) to Mo(I) Species.

Magnesium (about 0.1 g) was added to a solution of

$[Mo(CNC_6H_4CH_3-4)_2(dppe)_2](BF_4)_2$ (0.05 g) in thf (10 cm^3).

After stirring for 16 h, the solution was refluxed for about

4 h, then filtered and concentrated. Addition of ether then

gave $[Mo(CNC_6H_4CH_3-4)_2(dppe)_2]BF_4$ identified by its i.r.

spectrum (60%).

Reduction of Mo(I) to Mo(0) Species.

Lithium granules (0.08 g) were added to a solution of

$[Mo(CNC_6H_4CH_3-4)_2(dppe)_2]BF_4$ (0.06 g) in thf (15 cm^3).

After a few minutes the solution became very dark in colour

and its infra-red spectrum showed a peak at 1872 cm^{-1}, due

to the Mo(0) species. The solution was filtered, concentrated

and addition of ether then gave the dark reddish-brown product

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trans-[Mo(CNC$_6$H$_4$CH$_3$-4)$_2$(dppe)$_2$] identified by its i.r. spectrum.
(65%).

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