Cationic Metal Nitrosyl Complexes. Part 5.[1] Synthesis of Dinitrosylmolybdenum Compounds

Danielle Ballivet-Tkatchenko *
Institut de Recherches sur la Catalyse, C.N.R.S., 2 avenue Einstein, 69626 – Villeurbanne Cédex, France
Claude Bremard
Laboratoire de Spectrochimie Infrarouge et Raman, C.N.R.S., Bât. C.5, Université de Lille, 59655 Villeneuve d'Ascq Cédex, France

The reaction of $[Mo(NO)_2L_2Cl_2]$ [L = MeCN, PhCN, $CH_2{=}CHCN$, pyridine (py), or PPh_3; L_2 = 2,2′-bipyridine (bipy) or 1,2-bis(diphenylphosphino)ethane (dppe)] in 1,2-dimethoxyethane (dme) affords monocationic $[Mo(NO)_2L_2Cl(dme)]^+$ and dicationic $[Mo(NO)_2L_2(dme)_2]^{2+}$ species. The mechanism of chloride abstraction has been investigated by i.r., n.m.r., and u.v.–visible spectroscopy, conductimetry, and potentiometry. The dme solvates, when treated with nitriles or bipy, yield a series of cationic dinitrosylmolybdenum complexes. Some of the dicationic complexes catalyse the polymerisation of norbornadiene. The characterization of all new complexes is described.

Oligomerisation of dienes and activated olefins has been found to occur catalytically in the presence of cationic nitrosyl complexes derived from $[\{M(NO)_2Cl\}_2]$ (M = Co or Fe).[1-3] Abstraction of chloride is a prerequisite to observe activity, and the activity of the resulting solvated '$[M(NO)_2]^+$' species is due to (*i*) easy solvent–substrate exchange in the co-ordination sphere and (*ii*) further substrate activation, which is induced by the presence of the cationic charge, for the olefin polymerisation.[1] Chloride abstraction leads to unsaturated complexes and can be therefore considered as an activation process towards the formation of catalytic organometallic moieties.

We have extended the study of such unsaturated cationic complexes to $[\{Mo(NO)_2Cl_2\}_n]$. We report here the characterisation of mono- and di-cationic complexes. Their stabilisation has been achieved by addition of N- and P^{III}-donor ligands. Such species are active towards the polymerisation of norbornadiene.

Experimental

All reactions were carried out in the dark under an atmosphere of dry argon, and solvents were distilled under argon from appropriate drying agents. The compounds $[\{Mo(NO)_2Cl_2\}_n]$ (1), $[Mo(NO)_2(PPh_3)_2Cl_2]$ (2a), and $[Mo(NO)_2(py)_2Cl_2]$ (3a) (py = pyridine) were prepared by the literature methods.[4-6] The compounds $[Mo(NO)_2(MeCN)_2Cl_2]$ (4a), $[Mo(NO)_2(CH_2{=}CHCN)_2Cl_2]$ (5a), $[Mo(NO)_2(PhCN)_2Cl_2]$ (6a), $[Mo(NO)_2(dppe)Cl_2]$ (7a) [dppe = 1,2-bis(diphenylphosphino)ethane], and $[Mo(NO)_2(bipy)Cl_2]$ (8a) (bipy = 2,2′-bipyridine) were prepared by reaction of the free ligands, L or L_2, with (1).[7] The compounds gave satisfactory elemental analyses.

General Preparation of Monocationic Compounds $[Mo(NO)_2L_2L'Cl]Y$ (2b)—(8b) (Y = ClO_4, BF_4, *or* PF_6).—A typical preparation involved the complexes $[Mo(NO)_2L_2Cl(dme)]^+$ (dme = 1,2-dimethoxyethane) or $[Mo(NO)_2L_2Cl(Me_2CO)]^+$ as intermediates. Solid (2a)—(8a) (2 mmol) was suspended in freshly distilled dme or acetone (10 cm^3). AgY (2 mmol) was added slowly to the stirred suspension at room temperature. A green colour developed immediately in the solution. The mixture was stirred for *ca.* 6 h at room temperature, and then filtered through a glass frit and the solid (AgCl) washed with the solvent. Evidence of the formation of AgCl in quantitative yield (calc. weight of AgCl: 0.286 g; found after drying, 0.289 g) favours the cationic species in solution.

Attempted preparation of $[Mo(NO)_2(PPh_3)_2(MeCN)Cl][ClO_4]$ (2b). Acetonitrile (5 cm^3) was added to the dme solution containing the monocationic bis(phosphine) dme solvate. The mixture was stirred at room temperature for 1 h. Solvents were removed by distillation under reduced pressure. Taking the residual solid in a small volume of MeCN and adding diethyl ether to the resulting solution gave a green solid which was filtered off, washed with diethyl ether, and dried *in vacuo.*

$[Mo(NO)_2(py)_2(MeCN)Cl][ClO_4]$ (3b). The same procedure was followed starting from the bis(pyridine) dme monocationic solvate. Yield, 0.794 g (80%).

$[Mo(NO)_2(bipy)(MeCN)Cl][ClO_4]$ (8b). The same procedure was followed starting from the bipyridyl dme solvate. Yield, 0.878 g (90%) (Found: C, 29.3; H, 2.4; N, 14.0. Calc. for $C_{12}H_{11}Cl_2MoN_5O_6$: C, 29.5; H, 2.25; N, 14.35%).

$[Mo(NO)_2(MeCN)_3Cl][ClO_4]$ (4b). The same procedure was followed starting from the bis(acetonitrile) dme solvate. Addition of diethyl ether for recrystallisation failed and gave a green oil. A dark green solid was obtained from recrystallisation in nitromethane–diethyl ether (1 : 2). Yield, 0.540 g (60%) (Found: Mo, 22.4. Calc. for $C_6H_9Cl_2MoN_5O_6$: Mo, 23.2%).

$[Mo(NO)_2(CH_2{=}CHCN)_3Cl][ClO_4]$ (5b) and $[Mo(NO)_2(PhCN)_3Cl][ClO_4]$ (6b). These were prepared by a similar procedure to that used for (4b).

General Preparation of Dicationic Compounds $[Mo(NO)_2L_2L'_2]Y_2$ (2c)—(8c).—Solid (2a)—(8a) (2 mmol) was suspended in freshly distilled dme or acetone (10 cm^3). AgY (4 mmol) was added slowly to the stirred suspension. The mixture was allowed to stand for *ca.* 12 h at 40 °C; the solid AgCl was separated by filtration and washed with small amounts of solvent (calc. weight AgCl: 0.573 g; found, 0.552 g). The solution contained the dicationic $[Mo(NO)_2L_2(dme)_2]^{2+}$ or $[Mo(NO)_2L_2(Me_2CO)_2]^{2+}$ solvates.

$[Mo(NO)_2(PPh_3)_2(MeCN)_2][ClO_4]_2$ (2c). Acetonitrile (5 cm^3) was added to the dme solution containing the bis(phosphine) dme solvate. After 1 h reaction the solvents were removed under reduced pressure. The residual solid was taken up in a small volume of MeCN. Addition of diethyl ether gave a green solid which was filtered off, washed with diethyl ether, and dried *in vacuo*. Yield, 1.729 g (90%).

$[Mo(NO)_2(py)_2(MeCN)_2][ClO_4]_2$ (3c) was prepared by a similar procedure. Yield, 0.952 g (80%).

$[Mo(NO)_2(MeCN)_4][ClO_4]_2$ (4c). Tentative crystallisation by addition of diethyl ether gave a green oil. A dark green solid was obtained after several attempts of crystallisation with nitromethane–diethyl ether (1 : 2). Yield, 0.519 g (50%) (Found: Mo, 17.7. Calc. for $C_8H_{12}Cl_2MoN_6O_{10}$: Mo, 18.5%).

$[Mo(NO)_2(CH_2{=}CHCN)_4][ClO_4]_2$ (5c) was prepared by a similar procedure to that for (4c). Yield, 0.567 g (50%).

$[Mo(NO)_2(PhCN)_4][ClO_4]_2$ (6c) was prepared by a similar procedure to that for (4c). Yield, 0.795 g (70%) (Found: C, 40.5; H, 2.5. Calc. for $C_{28}H_{20}Cl_2MoN_6O_{10}$: C, 43.8; H, 2.6%).

$[Mo(NO)_2(bipy)(CH_3CN)_2][ClO_4]_2$ (8c) was prepared as above. Yield, 0.949 g (80%) (Found: C, 28.25; H, 2.7; N, 14.0. Calc. for $C_{14}H_{14}Cl_2MoN_6O_{10}$: C, 28.35; H, 2.35; N, 14.15%).

$[Mo(NO)_2(bipy)_2][ClO_4]_2$ was prepared by a method similar to that described in ref. 8. Yield, 0.800 g (60%).

Titrations of $[Mo(NO)_2L_2Cl_2]$ *with* $Ag[ClO_4]$.—The spectrophotometric titration of (4a) was carried out in acetone. Aliquots of $Ag[ClO_4]$ were added to solutions of (4a) (1.3×10^{-3} mol dm^{-3}) and the absorbance monitored after 12 h. The stoicheiometry of the reaction was deduced from the plot of absorbance (460 nm) *versus* the mol ratio $Ag[ClO_4]$:(4a).

The potentiometric titration of complexes (2a)—(8a) (1.3×10^{-3} mol dm^{-3}) at a silver electrode was carried out in acetonitrile (supporting electrolyte 0.1 mol dm^{-3} $[NEt_4][ClO_4]$) at 30 °C. Aliquots of $Ag[ClO_4]$ were added and the potential E of the Ag electrode was measured *versus* an Ag^+/Ag reference electrode.

The conductimetric titration of complexes (2a)—(8a) was carried out in nitromethane at 40 °C. Plots of (Λ/S cm^2 mol^{-1}) *versus* the mol ratio $Ag[ClO_4]$: complex established the stoicheiometry of the chloride abstraction.

Titrations of $[Mo(NO)_2L_2(MeCN)_2]^{2+}$ *with* NEt_4Cl.—The stoicheiometry of the reverse reactions was obtained from the spectrophotometric and conductimetric titrations at room temperature.

Spectroscopic Measurements.—U.v.–visible spectra were recorded on a Jobin-Yvon Duospac 203 spectrophotometer, i.r. spectra were recorded on a Perkin-Elmer 457 spectrometer with AgCl cells, and n.m.r. spectra were recorded on a Bruker WP 60 spectrometer operating at 60 MHz (^1H; $SiMe_4$ internal reference) and 24.3 MHz (^{31}P; 85% H_3PO_4 external reference; white-noise proton decoupling; chemical shifts to low field of the reference are designated positive). The elemental analyses were determined by the Microanalysis Laboratory of the C.N.R.S. **CAUTION:** perchlorate salts can be explosive and may detonate upon heating.

Results and Discussion

Two principal synthetic routes to cationic dinitrosyl complexes have been reported. These complexes can be prepared either by the reaction of NO^+ with neutral precursors [9–13] or by halide abstraction from neutral nitrosyl compounds by silver salts.[8,14–16]

Starting from $[Mo(NO)_2L_2Cl_2]$ (L = MeCN, PhCN, $CH_2{=}CHCN$, py, or PPh_3; L_2 = bipy or dppe), we have been able to generate the mono- and di-cationic dinitrosyl complexes through a metathetical exchange of Cl^- with a non-co-ordinating anion Y^- such as ClO_4^-, BF_4^-, or PF_6^-. These complexes are stable in solution in the solvated form $[Mo(NO)_2L_2(S)Cl]^+$ or $[Mo(NO)_2L_2(S)_2]^{2+}$ (S = solvent) and can be further stabilized by addition of one or two equivalents of neutral ligands, L′, leading to the replacement of S by L′.

Stoicheiometry of the Reaction Between $Ag[ClO_4]$ *and* $[Mo(NO)_2L_2Cl_2]$.—The abstraction of the chloro-ligands is achieved by addition of $Ag[ClO_4]$ in acetone, 1,2-dimethoxyethane, or MeCN at temperatures below 40 °C. The reaction takes place in two successive steps leading at first to the monocationic derivatives and then to the dicationic species in good yield [equations (i) and (ii); S = solvent].

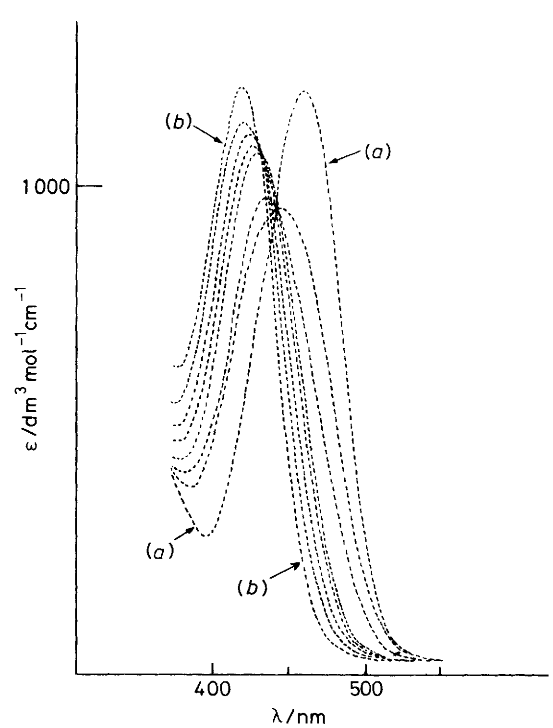


Figure 1. U.v.–visible spectra upon addition of $Ag[ClO_4]$ to an acetone solution of $[Mo(NO)_2(MeCN)_2Cl_2]$ (4a) at 25 °C, [Mo] = 1.3×10^{-3} mol dm^{-3}

$$\underset{(2a)—(6a),\ (8a)}{[Mo(NO)_2L_2Cl_2]} + Ag[ClO_4] \xrightarrow{S} \underset{(2b)—(6b),\ (8b)}{[Mo(NO)_2L_2(S)Cl][ClO_4]} + AgCl \qquad (i)$$

$$\underset{(2b)—(6b),\ (8b)}{[Mo(NO)_2L_2(S)Cl][ClO_4]} + Ag[ClO_4] \xrightarrow{S} \underset{(2c)—(6c),\ (8c)}{[Mo(NO)_2L_2(S)_2][ClO_4]_2} + AgCl \qquad (ii)$$

When the reactions (i) and (ii) are performed in CH_3CN solvent, the AgCl yield is not quantitative ($\leqslant 85\%$). In order to discard the participation of other reactions, *i.e.* ligand redistribution and redox steps, the formation of the cationic systems was followed by three complementary techniques: potentiometry, conductimetry, and u.v.–visible spectroscopy.

When increasing amounts of $Ag[ClO_4]$ are added to a CH_3CN solution of $[Mo(NO)_2(bipy)Cl_2]$ (8a) the potentiometric titration of Ag^+ at a silver electrode shows that two moles of silver salt react with one mole of (8a). According to the same procedure, the conductimetric titration of (8a) or $[Mo(NO)_2(py)_2Cl_2]$ (3a) with $Ag[ClO_4]$ reveals that two conducting complexes are successively formed. The first one corresponds to a 1 : 1 electrolyte and the second to a 2 : 1 electrolyte.[17] The consumption of $Ag[ClO_4]$ exactly corresponds to the 1 : 1 and 2 : 1 stoicheiometries. Typical changes in the u.v.–visible spectra are reported in Figure 1 for $[Mo(NO)_2(MeCN)_2Cl_2]$ (4a), when increasing amounts of $Ag[ClO_4]$ are added. The existence of two isosbestic points

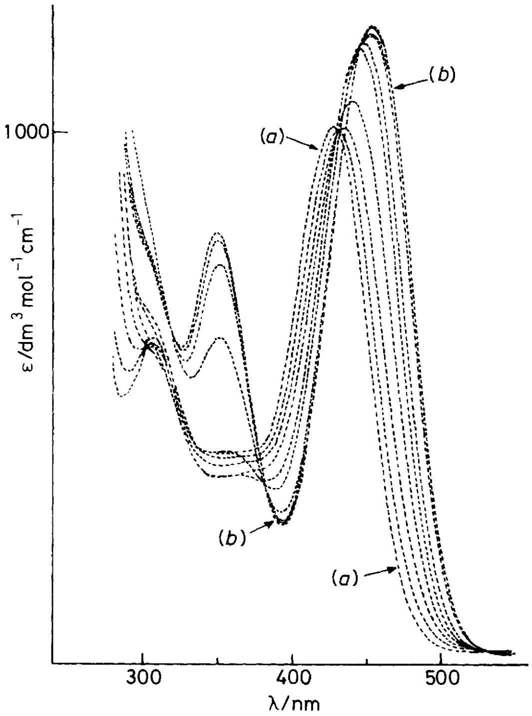


Figure 2. U.v.-visible spectra upon addition of NEt_4Cl in an acetonitrile solution of $[Mo(NO)_2(MeCN)_4]^{2+}$, (4c) at 25 °C, [Mo] = 1.1×10^{-3} mol dm^{-3}

suggests that the absorption is accounted for by three species. Curve (*a*) is characteristic of compound (4a) ($\lambda_{max.}$ = 460 nm) and curve (*b*) of the dicationic complex (4c) ($\lambda_{max.}$ = 420 nm). The monocationic complex, (4b), absorbs at intermediate wavelength ($\lambda_{max.}$ = 430 nm). These assignments are confirmed by comparison with spectra of the pure cationic derivatives. The addition of $Ag[ClO_4]$ [Ag^+ : (4a), 1 : 1] favours at first the formation of the monocationic complex, the dicationic species appearing at higher ratios of Ag^+ : (4a).

From these experiments it can be concluded that the chloro-ligand abstraction [equations (i) and (ii)] leads to the quantitative and successive formations of the mono- and di-cationic complexes. The non-quantitative precipitation of AgCl in MeCN is probably linked to the presence of some colloidal AgCl, as the solubility product (1.3×10^{-13} mol^2 dm^{-6}) and soluble $AgCl_2^-$ concentration cannot account for the difference found.[18]

The preparation method involving dme solvates as intermediates was further employed. The dme solvent is a convenient leaving group, and, once the solvates are formed, the addition of ligand L′ allows the cationic complexes to be isolated without requiring further purification. Successfully prepared by this procedure are the complexes formed with L′ = RCN and L'_2 = bipy. Attempts with L′ = PPh_3 and L'_2 = dppe under comparable conditions failed, and lead to the loss of the nitrosyl ligand.

Characterization of the Cationic Complexes.—The cationic materials are very hygroscopic and the perchlorate derivatives are often explosive under the conditions of elemental analyses so that satisfactory data have only been obtained in some instances. Nevertheless this anion was used in this work, as changing to PF_6^- or BF_4^- anions induces secondary reactions by loss of fluorine. For example, a crude solution of $[Mo(NO)_2(MeCN)_4][PF_6]_2$ exhibits in the ^{31}P n.m.r. (relative to H_3PO_4) spectrum a septet due to PF_6^- [δ − 144.9 p.p.m., *J*(P–F) = 700 Hz] together with a triplet assigned to $O_2PF_2^-$ [δ − 20.6 p.p.m., *J*(P–F) = 1 010 Hz] in agreement with previous reported data.[19–21] The estimated PF_6^- : $O_2PF_2^-$ ratio is around 10 : 1. On the other hand, a crude solution of $[Mo(NO)_2(PPh_3)_2(CH_3CN)_2][PF_6]_2$ only exhibits the PF_6^- septet over one hour reaction.

To check the purity and the yield of the cationic complexes with ClO_4^- anion, back-titration with the soluble NEt_4Cl salt was performed and followed by u.v.-visible spectroscopy (Figure 2). Reactions (i) and (ii) are totally reversed by adding stoicheiometric amounts of soluble Cl^- salts at 25 °C.

The characterization of the cationic complexes has been achieved by i.r., u.v.-visible and n.m.r. spectroscopies, and conductimetry (Table). The stereochemistry of some complexes has been determined by i.r. and n.m.r., and varies according to the nature of ligand L.

I.r. and Electronic Spectra.—The i.r. spectra of all the complexes exhibit two strong bands in the ν(NO) region (1 850—1 650 cm^{-1}) which indicate that the NO ligands are mutually *cis* in the octahedral geometry.[7,22] The ν(NO) values (Table) are increased by *ca.* 30 cm^{-1} in going from the neutral complexes (2a)—(8a) to the monocations (2b)—(8b), to the dication (2c)—(8c). Therefore Mo–NO back-donation logically decreases as the positive charge increases. This effect is also seen in the electronic spectra. Some typical spectra of the octahedral complexes are shown in Figures 1 and 2. An intense absorption at *ca.* 440 nm (ε *ca.* 1 000 dm^3 mol^{-1} cm^{-1}) is present for all the complexes (Table). Very similar values have been obtained for another series of octahedral $[Mo(NO)_2L_2X_2]$ [23] (L = $PEtPh_2$, PEt_3, or PBu^n_3; X = Cl, Br, or NCS) derivatives. Although assignments of the electronic transitions have not been reported on this type of compound, it seems that the absorption at *ca.* 440 nm can be assigned to metal $\longrightarrow \pi^*$(NO) transition. This band is not very sensitive to the nature of the co-ligands L but when the cationic charges appear on the complexes a shift to higher energies is observed. This result agrees with the stabilization of metal *d* orbitals when the cations are formed and causes less π interactions with the NO ligands, as also revealed by i.r. ν(NO) changes.

The i.r. spectra display also informative bands in the ν(C≡N) region (L = MeCN, PhCN, or CH_2=CHCN) and ν(Cl–O) of ClO_4^-. The ν(C≡N) stretching frequencies for the MeCN and PhCN derivatives indicate the classical co-ordination through the nitrogen atom [14] (Table). In the case of the ligand CH_2=CHCN two co-ordination sites are available: the nitrogen atom and the olefinic bond. Both types of co-ordination are already known. Electron-deficient metal ions induce the co-ordination of CH_2=CHCN through the nitrogen atom and this is the case in the present molybdenum complexes (5b) and (5c). The ν(C≡N) shifts to high frequency and the characteristic C–H vibrations are not perturbed by comparison with those of the free ligand.[14] For the cationic complexes, the counter anion ClO_4^- exhibits two bands centred at 1 095s br and 630m cm^{-1}, consistent with a T_d symmetry [24] which indicates no interaction with the cation either in solution or in the solid state. Replacing ClO_4^- by PF_6^- or BF_4^- also leads to ionic systems if the reaction is continued for one hour. Over a longer reaction time, the i.r. spectrum indicates that fluorine may bind weakly to molybdenum. When chloride abstraction is carried out on complex (2a) with $Ag[BF_4]$ in CH_2Cl_2 solution, a new solid is obtained by addition of hexane. Although the product cannot be well characterized, the co-ordination of the counter anion is supported by comparison of data on other systems.

*Hydrogen-*1 *and Phosphorus-*31 *N.M.R. Data.*—Representative ^1H n.m.r. data were obtained for most of the complexes prepared in the present work (Table).

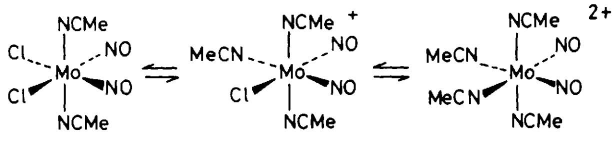
Table. Characteristic i.r., u.v.–visible, ^{1}H n.m.r., and conductance data for cationic dinitrosylmolybdenum complexes

Complex	ν_{sym}(NO) [a]/ cm^{-1}	ν_{asym}(NO) [a]/ cm^{-1}	ν(C≡N) [a]/ cm^{-1}	$\lambda_{max.}$ [a]/ nm	^{1}H n.m.r.[b]/(δ/p.p.m.) (methyl)	other	Λ_0 [c]/S cm^2 mol^{-1}
(2c) $[Mo(NO)_2(PPh_3)_2(MeCN)_2][ClO_4]_2$	1 805s	1 690s	2 330, 2 300w	430	2.2 (6 H)	7.43—7.96 (m, 30 H)	
(3b) $[Mo(NO)_2(py)_2(MeCN)Cl][ClO_4]$	1 810s	1 690s	2 330, 2 300w	435			
(3c) $[Mo(NO)_2(py)_2(MeCN)_2][ClO_4]_2$	1 830s	1 720s	2 330, 2 300w	430			
(4b) $[Mo(NO)_2(MeCN)_3Cl][ClO_4]$	1 830s	1 720s	2 330, 2 300w	430			125
$[Mo(NO)_2(MeCN)_3Cl][PF_6]$	1 830s	1 720s	2 330, 2 300w	430	2.51 (9 H) [d]		
(4c) $[Mo(NO)_2(MeCN)_4][ClO_4]_2$	1 860s	1 750s	2 330, 2 300w	420			215
$[Mo(NO)_2(MeCN)_4][PF_6]_2$	1 855s	1 750s	2 330, 2 300w	420	2.60 (12 H) [d]		
$[Mo(NO)_2(MeCN)_4][BF_4]_2$	1 855s	1 750s	2 330, 2 300w	420			
(5b) $[Mo(NO)_2(CH_2{=}CHCN)_3Cl][ClO_4]$	1 830s	1 720s	2 280m	435		6.05—7.15 (m, 9 H)	120
(5c) $[Mo(NO)_2(CH_2{=}CHCN)_4][ClO_4]_2$	1 850s	1 730s	2 280m	420		6.20—7.30 (m, 12 H)	220
$[Mo(NO)_2(CH_2{=}CHCN)_4][PF_6]_2$	1 850s	1 730s	2 280m	420			
$[Mo(NO)_2(CH_2{=}CHCN)_4][BF_4]_2$	1 850s	1 730s	2 280m	420			
(6b) $[Mo(NO)_2(PhCN)_3Cl][ClO_4]$	1 830s	1 720s	2 280m	432		7.46—8.10 (m, 15 H)	120
(6c) $[Mo(NO)_2(PhCN)_4][ClO_4]_2$	1 850s	1 750s	2 300m	420		7.46—8.13 (m, 20 H)	230
(8b) $[Mo(NO)_2(bipy)(MeCN)Cl][ClO_4]$	1 810s	1 700s	2 330, 2 300w	435	2.66 (3 H)	7.80—9.97 (m, 8 H)	103
$[Mo(NO)_2(bipy)(MeCN)Cl][BF_4]$	1 810s	1 700s	2 330, 2 300w	435			
(8c) $[Mo(NO)_2(bipy)(MeCN)_2][ClO_4]_2$	1 830s	1 730s	2 330, 2 300w	428	2.78 (6 H)	7.83—9.17 (m, 8 H)	208
$[Mo(NO)_2(bipy)_2][ClO_4]_2$	1 830s	1 730s		430		7.40—9.23 (m, 16 H)	180
$[Mo(NO)_2(bipy)_2][PF_6]_2$	1 830s	1 730s					
$[Mo(NO)_2(bipy)_2][BF_4]_2$	1 830s	1 730s		430			

[a] In CH_2Cl_2. [b] In $CDCl_3$ at 30 °C. [c] In $MeNO_2$ at 25 °C. [d] From ref. 8.

For the acrylonitrile derivatives (5b) and (5c), resonances at 5.77—7.50 p.p.m. are assigned to vinyl protons. For the benzonitrile derivatives (6b) and (6c), multiplets around 7.7 p.p.m. are due to the aromatic protons. For the acetonitrile derivatives (4b) and (4c) only one signal occurs at *ca.* 2.5 p.p.m. The stereochemical arrangement of acetonitrile around the *cis*-$Mo(NO)_2$ fragment has been discussed previously.[8,11] For compound (4b), it is suggested that one MeCN ligand (easily exchangeable) occupies a *trans* position to one NO group, the chloro-ligand being *trans* to the other NO group.[8] This assignment is in agreement with our results taking into account the structure of the neutral precursor (4a) determined on the basis of ^{1}H n.m.r. and far-i.r. spectra.[7] The two chloro-ligands are *trans* to the NO groups and the MeCN ligands do not interchange on the n.m.r. time-scale. Therefore, Scheme 1 is proposed for chloride abstraction.

Mixed-ligand complexes have also been characterised. The complex (2c) is prepared from the precursor *cis-trans-cis*-$[Mo(NO)_2(PPh_3)_2Cl_2]$ (2a). The ^{31}P n.m.r. spectrum of (2c) exhibits one singlet at 51.3 p.p.m. in CD_3CN. The ^{1}H n.m.r. spectrum shows a multiplet at 7.7 p.p.m. (30 H, aromatic protons) and a sharp singlet at 2.2 p.p.m. (6 H, methyl protons) in $CDCl_3$. In CD_3CN a relatively fast exchange occurs with co-ordinated CH_3CN. On these grounds we suggest that (*i*) the two equivalent phosphine ligands remain in a *trans* position, as for the neutral precursor (2a), and that (*ii*) the two exchangeable acetonitriles are *trans* to the NO groups. Such a situation is also proposed for the complexes (4a), (4b), and (4c) (Scheme 1).

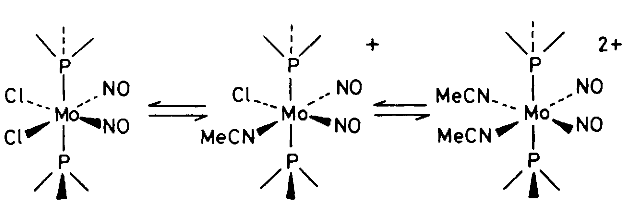


(4a) (4b) (4c)

Scheme 1.

The monocationic complex (2b) cannot be obtained in a pure form. A ^{31}P n.m.r. study reveals a redistribution of the chloro-ligand in order to form in equal amounts the dichloro-complex (2a) and the dicationic complex (2c). Three singlets are observed at 48.1, 46.9, and 51.3 p.p.m. of relative intensities x: $1-2x$: x [x = mol fraction of (2a) or (2c)] which are assigned to species (2a), (2b), and (2c) respectively. According to these results, Scheme 2 reports the structures for these three complexes.

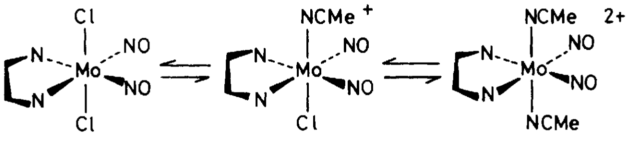
With the chelating ligand bipy, different structures are found. The *X*-ray structure determination of $[Mo(NO)_2(bipy)Cl_2]$ (8a), shows a *cis,cis,trans* arrangement.[7] The abstraction of one chloro-ligand in the presence of acetonitrile leads to (8b), which exhibits ^{1}H n.m.r. resonances at 7—9 (8 H, bipy) and at 2.66 p.p.m. (3 H, MeCN). The cor-



(2a) (2b) (2c)

Scheme 2.

responding dicationic complex (8c) exhibits resonances at 7—9 (8 H, bipy) and at 2.78 p.p.m. (6 H, two equivalent MeCN). In this case no fast exchange occurs in CD_3CN for either compounds (8b) and (8c) in contrast to the situation encountered for (4b) and (2c). Therefore we propose that CH_3CN does not occupy a *trans* position to the NO groups. The chloride abstraction mechanism is shown in Scheme 3.



(8a) (8b) (8c)

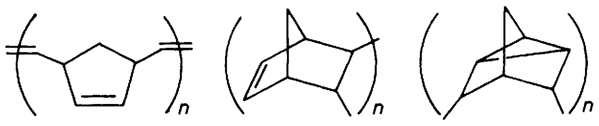
Scheme 3.

Schemes 1—3 establish that the chloride abstraction occurs without any ligand rearrangement in the co-ordination sphere. Nevertheless, such rearrangement proceeds with suitable ligands. $[Mo(NO)_2(bipy)_2]^{2+}$ can be prepared from (8c) and (4c) by addition of bipy at room temperature. From the precursor (8c) a ligand rearrangement has to occur and the exchange process can be easily monitored by i.r., whereas from the precursor (4c) the reaction is straightforward.

Attempts to obtain olefin-containing cationic complexes failed. Nevertheless, the co-ordination of olefin does occur as evidenced by catalytic experiments. Some of the complexes exhibit catalytic properties towards norbornadiene polymerisation.

Norbornadiene Polymerisation.—The dichloro molybdenum precursors are not active in the polymerisation of norbornadiene. Addition of the silver salt in the ratio $Ag^+ : Mo$ of 2 : 1 initiates the reaction. Correlation between norbornadiene conversion and u.v.–visible spectra of the reacting solution containing precursor (2a) or (4a) shows that norbornadiene is polymerised when the dicationic complex is formed. Two co-ordination sites in a *cis* position are therefore available for diene activation.

Catalytic runs were carried out in non-co-ordinating solvent (CH_2Cl_2 or $ClCH_2CH_2Cl$) between 25 and 70 °C during 12 h for a catalyst : monomer ratio of 1 : 100. Conversion up to 90% is obtained at 40 °C and does not depend upon the ligand L (PPh_3 or MeCN) present in the precursor $[Mo(NO)_2L_2Cl_2]$. From the reaction medium two polymers are isolated: one is insoluble in common organic solvents (63% yield) and the other is soluble in benzene (37% yield). The soluble fraction exhibits ^1H n.m.r. resonances only in the region 1—2 p.p.m. indicating the loss of olefinic bonds. The i.r. spectra of both polymers in KBr pellets also indicate the loss of olefinic bonds (no band in the 1 500—1 800 cm^{-1} region) whereas a characteristic band centred at 800 cm^{-1} together with one centred at 3 050 cm^{-1} are present. Previous studies on norbornadiene polymerisation have shown that different structures can be found according to the catalytic system in Scheme 4.



I II III

Scheme 4.

Structure I is observed with a metathesis catalyst [25] whereas structures II and III are observed with palladium(II) complexes [26] and with cationic initiators respectively.[27] These three structures display characteristic ^1H n.m.r. and i.r. spectra. Only structure III exhibits a set of intense bands at 3 050 and 800 cm^{-1} due to the nortricyclene framework.[28] The presence of such bands in our system together with the absence of olefinic features support structure III for the polynorbornadiene. The common structure found with cationic initiators [27] and with the dicationic molybdenum nitrosyl complexes described in this paper could indicate a similar reaction mechanism involving carbocations. Hence, norbornadiene co-ordinated to Mo^{2+} ions would be sufficiently strongly electrophilic so as to induce the norbornen-3-yl carbenium ion formation and rearrangement that initiates cationic chain propagation. Such properties of co-ordinated olefins have been investigated in detail with cationic nitrosyl complexes of iron and cobalt.[3] We have shown that polymerisation occurs through carbocation formation. Other cationic complexes such as $[Pd(MeCN)_4]^{2+}$ are also able to initiate cationic polymerisation reactions.[29] Therefore it appears that with cationic complexes the mechanism of the catalytic cycle is dictated by the electrophilicity of the co-ordinated unsaturated substrate. A high extent of cationic charge delocalisation onto the substrate induces cationic reactions whereas in the case of less charge transfer a typical co-ordination-sphere mechanism is operating. For example, norbornadiene undergoes cyclodimerisation with the $[Co(NO)_2S_n]^+$ (S = solvent) system [1] whereas polymers are formed with the $[Mo(NO)_2L_2S_n]^{2+}$ system. Thus, norbornadiene co-ordinated to Mo^{2+} ions is more electrophilic than when it is co-ordinated to Co^+.

Acknowledgements

We would like to thank Dr. I. Tkatchenko for helpful discussions.

References

1 D. Ballivet and I. Tkatchenko, *J. Mol. Catal.*, 1975, **1**, 319.
2 D. Ballivet, C. Billard, and I. Tkatchenko, *J. Organomet. Chem.*, 1977, **124**, C9.
3 D. Ballivet-Tkatchenko, C. Billard, and A. Revillon, *J. Polym. Sci., Polym. Chem. Ed.*, 1981, **19**, 1967.
4 (*a*) M. W. Anker, R. Colton, and I. B. Tomkins, *Aust. J. Chem.*, 1968, **21**, 1149; (*b*) B. F. G. Johnson and F. A. Cotton, *Inorg. Chem.*, 1964, **3**, 1609.
5 W. B. Hughes and E. A. Zuech, *Inorg. Chem.*, 1973, **12**, 471.
6 L. Bencze, *J. Organomet. Chem.*, 1973, **56**, 303.
7 D. Ballivet-Tkatchenko, C. Bremard, F. Abraham, and G. Nowogrocki, preceding paper.
8 B. F. G. Johnson, Abul Khair, C. G. Savory, R. H. Walter, K. H. Alobaidi, and T. J. Al Hassam, *Transition Met. Chem.*, 1978, **3**, 81.

9 B. F. G. Johnson, S. Bhaduri, and N. G. Connelly, *J. Organomet. Chem.*, 1972, **40**, 6.
10 N. G. Connelly, *J. Chem. Soc., Dalton Trans.*, 1973, 2183.
11 M. Green and S. H. Taylor, *J. Chem. Soc., Dalton Trans.*, 1972, 2629.
12 G. Dolcetti, N. W. Hoffman, and J. P. Collman, *Inorg. Chim. Acta*, 1972, **6**, 531.
13 N. G. Connelly, P. T. Draggett, M. Green, and T. A. Kuc, *J. Chem. Soc., Dalton Trans.*, 1977, 70.
14 D. Ballivet and I. Tkatchenko, *Inorg. Chem.*, 1977, **16**, 945.
15 F. J. Regina and A. Wojcicki, *Inorg. Chem.*, 1980, **19**, 3803.
16 M. Ghedini, G. Dolcetti, O. Gandolfi, and B. Giovamitti, *Inorg. Chem.*, 1976, **15**, 2385.
17 W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81.
18 R. Alexander, E. C. F. Ko, Y. C. Mac, and A. J. Parker, *J. Am. Chem. Soc.*, 1967, **89**, 3703.
19 S. J. Thomson, P. M. Bailey, C. White, and P. M. Maitlis. *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 490.
20 D. Condon, M. F. Deane, J. Labor, N. G. Connelly, and A. C. Lewis, *J. Chem. Soc., Dalton Trans.*, 1977, 925.
21 N. G. Connelly and C. Gardner, *J. Chem. Soc., Dalton Trans.*, 1979, 609.
22 M. O. Visscher and K. G. Caulton, *J. Am. Chem. Soc.*, 1972, **94**, 5923.
23 T. Nimry, M. A. Urbanic, and R. A. Walton, *Inorg. Chem.*, 1979, **18**, 691.
24 B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 1961, 3091.
25 L. Reif and H. Höcker, *Makrol. Chem.*, 1981, **2**, 745.
26 A. Sen and Ta-Wang Lai, *Organometallics*, 1982, **1**, 415.
27 J. P. Kennedy and J. A. Hinlicky, *Polymer*, 1965, **6**, 133.
28 G. E. Pollard, *Spectrochim. Acta*, 1962, **18**, 837.
29 A. Sen and Ta-Wang Lai, *J. Am. Chem. Soc.*, 1981, **103**, 4627.

Received 1*st October* 1982; *Paper* 2/1691