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Cyanoimide-Bridged, Bi- and Trinuclear, Heterometallic Complexes with an NCN–Mo–NCN Phosphinic Core

Sónia M. P. R. M. Cunha,[a] M. Fátima C. Guedes da Silva,*[a,b]
João J. R. Fraústo da Silva,[a] and Armando J. L. Pombeiro*[a]

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The heterometallic dinuclear complexes of the types *trans*-[Mo(NCN)(dppe)$_2$(μ-NCN)M] [M = WCl$_4$(PPh$_3$), ReOCl$_3$(PPh$_3$) or *mer*-ReCl(N$_2$)(PMePh$_2$)$_3$; dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$] and [Mo(NCN)(dppe)$_2$(μ-NCN)M][BF$_4$]Br [M = *trans*-Fe(NCC$_6$H$_4$NO$_2$-4)(depe)$_2$; depe = Et$_2$PCH$_2$CH$_2$PEt$_2$] and the trinuclear ones [Mo(dppe)$_2${(μ-NCN)M}$_2$] [M = VCl$_3$(thf) or PtCl$_2$(PEt$_3$)] were prepared by reaction of the bis(cyanoimido)molybdenum complex *trans*-[Mo(NCN)$_2$(dppe)$_2$] with the corresponding transition-metal Lewis acid (M) precursors, particularly [VCl$_3$(thf)$_3$], [WCl$_4$(PPh$_3$)$_2$], [ReOCl$_3$(PPh$_3$)$_2$], *trans*-[ReCl(N$_2$)(PMePh$_2$)$_4$], *trans*-[FeBr(NCC$_6$H$_4$NO$_2$-4)(depe)$_2$][BF$_4$] and [Pt$_2$Cl$_4$(PEt$_3$)$_2$]. These adducts were characterized by FTIR, ^{1}H, ^{13}C and ^{31}P{^{1}H} NMR spectroscopy, mass spectrometry and cyclic voltammetry.

Introduction

Cyanamide (N≡C–NH$_2$) is a simple unsaturated species isoelectronic with N$_2$ and is also a substrate of nitrogenase[1a] with both scientific and industrial interest.[1–5] In spite of its developed organic chemistry, examples of the coordination of N≡C–NH$_2$ to transition-metal centres are still scarce,[6–16] contrasting with the related organonitriles (N≡C–R), whose coordination chemistry has been extensively investigated and reviewed.[17–20]

Following our interest in the activation of alternative substrates of nitrogenases by metal centres, for example, molybdenum (present in the conventional nitrogenase), we unexpectedly obtained the cyanoimide (N=C=N^{2-}) complex of Mo^{IV} *trans*-[Mo(NCN)$_2$(dppe)$_2$] (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) upon treatment of the dinitrogen Mo^0 complex *trans*-[Mo(N$_2$)$_2$(dppe)$_2$] with cyanamide.[6,7] This substrate underwent reductive dehydrogenation to the cyanoimide form. The still underdeveloped chemistry of the cyanoimide ligand has recently been the object of attention and different synthetic ways of generating cyanoimide complexes have been reported, for example, NCN abstraction from the bicyclic cyanoamine 2,3:5,6-dibenzo-7-azabicyclo-[2.2.1]hepta-2,5-diene (NCdbabh),[21a] salt metathesis reactions of dipotassium cyanamide, K$_2$(NCN),[21b] or cyanation of nitrido complexes.[21c]

At Os^{IV}, the cyanoimide ligand can behave as an oxido analogue, as PPh$_3$ or alkenes add to the coordinated cyanoimide in the osmium complexes *trans*-[Os(NCN)(Cl)$_2$(tpy)] or *mer*-[Os(NCN)(Cl)$_3$(bpy)]$^-$ (tpy = 2,2′:6′,2′′-terpyridine; bpy = 2,2′-bipyridine) to afford cyanoiminophosphorane and cyanoaziridine complexes, respectively.[21c]

The cyanoimide ligand can also act as a Lewis base towards Lewis acid metal species, thus behaving as a linker of transition-metal units in μ-NCN complexes. These can be obtained directly upon reaction with a NCN^{2-} source, as observed for the homodinuclear compounds [{M(NRAr)$_3$}$_2$(μ-NCN)] (M = Mo, R = *i*Pr; M = V or U, R = *t*Bu) formed upon NCN abstraction from the bicyclic cyanoamine NCdbabh (see above) by the corresponding metal fragments,[21a] and for [{Cp*WS$_2$}$_2$(μ-NCN)][21b] (Cp* = η^5-C$_5$Me$_5$), [{(bipy)$_2$Co}$_2$(μ-NCN)$_2$][ClO$_4$]$_2$[21b] and the bis(cyanoimido)-capped triruthenium compound Na-[(Cp*Ru)$_3$(μ$_3$-NCN)$_2$],[21d] which were prepared directly from salt metathesis reaction with bis(alkali metal) cyanamide. All these products are homometallic complexes, but heterometallic species should be achieved if stepwise reactions would be performed with different metal centres at distinct steps, and this constitutes the object of the current study.

The basicity of the terminal N atom of the NCN ligand in the above bis(cyanoimido) complex *trans*-[Mo(NCN)$_2$(dppe)$_2$] has already been proven, as it is susceptible to attack by various electrophiles E$^+$ (proton or organocation), affording the corresponding mononuclear adducts *trans*-[Mo(NCN)(NCNE)(dppe)$_2$]$^+$.[7] We have now extended the study of the basicity of the cyanoimide ligands in such a

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[a] Centro de Química Estrutural, Complexo Interdisciplinar, Instituto Superior Técnico, TU Lisbon,
Av. Rovisco Pais, 1049-001 Lisboa, Portugal
E-mail: pombeiro@ist.utl.pt
[b] Universidade Lusófona de Humanidades e Tecnologias, ULHT Lisbon,
Campo Grande 376, 1749-024, Lisboa, Portugal
E-mail: fatima.guedes@ist.utl.pt

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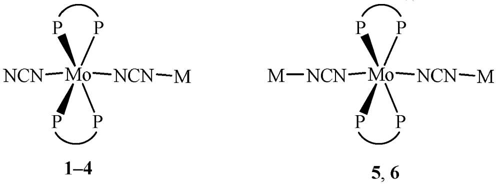
bis(cyanoimido) complex towards several transition-metal Lewis acids of the periodic groups 5–8 and 10 and succeeded in preparing various di- or trinuclear heterometallic adducts with the bridging NCN unit. The syntheses and spectroscopic characterization of these novel complexes exhibiting one or two cyanoimide bridges by IR, multinuclear NMR and FAB-MS techniques are reported.

Results and Discussion

Treatment of a CH_2Cl_2 (or THF) solution of *trans*-[Mo(NCN)$_2$(dppe)$_2$] with an equimolar amount of the appropriate Lewis acid precursor, [$WCl_4(PPh_3)_2$], [$ReOCl_3(PPh_3)_2$], *trans*-[ReCl(N_2)($PMePh_2$)$_4$] or *trans*-[FeBr($NCC_6H_4NO_2$-4)(depe)$_2$][BF_4] (depe = $Et_2PCH_2CH_2PEt_2$), results in the formation of the corresponding heterodinuclear adducts *trans*-[Mo(NCN)(dppe)$_2$(μ-NCN)WCl_4(PPh_3)] (**1**), *trans*-[Mo(NCN)(dppe)$_2$(μ-NCN)$ReOCl_3$(PPh_3)] (**2**), *trans*-[Mo(NCN)(dppe)$_2$(μ-NCN)ReCl(N_2)($PMePh_2$)$_3$] (**3**) or *trans*-[Mo(NCN)(dppe)$_2$(μ-NCN)Fe($NCC_6H_4NO_2$-4)(depe)$_2$][BF_4]Br (**4**) with a bridging NCN ligand. The trinuclear species with two bridging NCN moieties [Mo(dppe)$_2${(μ-NCN)VCl_3(thf)}$_2$] (**5**) and [Mo(dppe)$_2${(μ-NCN)$PtCl_2$(PEt_3)}$_2$] (**6**) are formed when using 2 equivalents of [VCl_3(thf)$_3$] or 1 equivalent of the platinum dimer [$Pt_2Cl_4(PEt_3)_2$], respectively. The formation of the adducts (Schemes 1 and 2) involves ligand displacement from the Lewis acid precursor as shown by the observation of the $^{31}P\{^1H\}$ NMR singlet of the liberated phosphane in the cases of the synthesis of the appropriate adducts.

All complexes were isolated as coloured solids and, with the exception of trinuclear adduct **5**, are diamagnetic. The proposed formulations and geometries were assigned on the basis of IR, ^1H NMR and $^{31}P\{^1H\}$ NMR spectroscopy, elemental analysis, MS (FAB) spectrometry and cyclic voltammetry. The considerable instability in solution of the adducts (with the exception of **6**) precluded the acquisition of reliable ^{13}C NMR spectroscopic data.

In their IR spectra, ν_{as}(N=C=N) and ν_s(N=C=N) appear as strong or very strong bands in the 2090–2030 and 1338–1279 cm^{-1} ranges, respectively. In the trinuclear adducts, these bands occur at slightly higher wavenumbers than in the binuclear ones. However, the generality of this observation cannot be established in view of the limited number of examples. Moreover, the change in ν_{as}(N=C=N) upon formation of the adduct(s) is insignificant, as observed, for example, for the pair [Cp*WS_2(NCN)] and [{Cp*WS_2}$_2$(μ-NCN)],[21b] with ν_{as} at 2083 and 2087 cm^{-1}, respectively. Such values of our complexes are comparable to those found for the parent bis(cyanoimido) Mo complex (2043 and 1279 cm^{-1})[6] or in [{Cp*WS_2}$_2$(μ-NCN)] (ν_{as} 2087 cm^{-1}),[21b] and the former ν_{as} stretch is higher than that observed in [{(bipy)$_2$Co}$_2$(μ-NCN)$_2$][ClO_4]$_2$ (ν_{as} 1943 cm^{-1})[21b] and lower than that in the bis(cyanoimido)-capped triruthenium compound Na[(Cp*Ru)$_3$(μ_3-NCN)$_2$] (ν_{as} 2111 cm^{-1}).[21d]

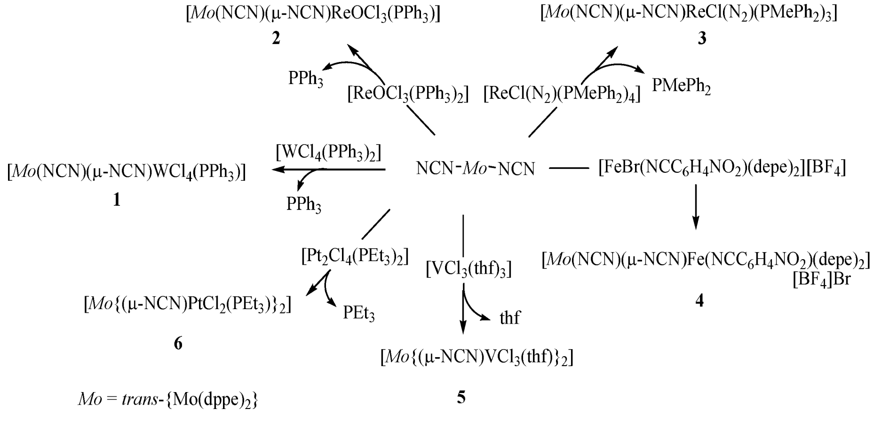


P⌒P = dppe; M = $WCl_4(PPh_3)$ (**1**), $ReOCl_3(PPh_3)$ (**2**), $ReCl(N_2)(PMePh_2)_3$ (**3**), Fe($NCC_6H_4NO_2$-4)(depe)$_2$ (**4**), VCl_3(thf) (**5**) or $PtCl_2(PEt_3)$ (**6**)

Scheme 2.

Other characteristic bands are as follows: 965 [ν(Re=O)] in **2**; 1920 [ν(N≡N)] in **3**; 2175 [ν(N≡C)], 1518 [ν_{as}(NO_2)], 1338 [ν_s(NO_2)], 1160–1000 [ν(B–F)]cm^{-1} in **4**. The changes in ν(N≡N) and in ν(N≡C) upon formation of adducts **3** and **4**, for [ReCl(N_2)($PMePh_2$)$_4$] and [FeBr($NCC_6H_4NO_2$)(depe)$_2$]$^+$, respectively, are not appreciable.

The singlet observed in the $^{31}P\{^1H\}$ NMR spectra (in CD_2Cl_2) of all adducts at δ values ranging from –102.7 to –105.4 ppm is due to the four equivalent phosphorus nuclei of the Mo-bound dppe ligands, being close to that (δ = –102.2 ppm)[6] shown by the parent bis(cyanoimido) complex. An additional singlet, with the appropriate relative intensity, is detected in **1** (δ = –95.1 ppm; ^{183}W satellites, $J_{P,W}$ = 308.9 Hz, *P*Ph_3), in **2** (δ = –175.0 ppm, *P*Ph_3), in **4** (δ =



Scheme 1.

–79.8 ppm, depe) and in **6** (δ = –144.6 ppm; ^{195}Pt satellites, $J_{\mathrm{P,Pt}}$ = 3660 Hz, *P*Et$_3$). In compound **3**, the observed AB$_2$ spin system (triplet and doublet at δ = –169.0 and –167.5 ppm, respectively, $^{2}J_{\mathrm{PA,PB}}$ = 9.7 Hz) for the three PMePh$_2$ at the Re centre indicates the meridional configuration of these phosphane ligands.

Although in the FAB+ mass spectra of the adducts, run in 3-nitrobenzyl alcohol (NOBA) matrices, the corresponding molecular ions M$^+$ are not observed, a common type of decomposition route is followed involving the rupture of the NCN→M bond (only one of these bonds is initially cleaved for trinuclear compound **6**). The fragment ion [Mo(NCN)$_2$(dppe)$_2$]$^+$ (*m*/*z* = 974) is detected in all cases, as well as those involving the other metal centres. Relevant fragment ions were identified with one (for the dinuclear) or two (for the trinuclear) metal ions (see Experimental Section). The experimental isotopic patterns of the most prominent and typical clusters closely match the simulated ones (Supporting Information, Figure S1).

The study, by cyclic voltammetry (CV), of the redox properties of the adducts [Mo(NCN)(dppe)$_2$(μ-NCN)-ReCl(N$_2$)(PMePh$_2$)$_3$] (**3**) and [Mo(dppe)$_2${(μ-NCN)PtCl$_2$-(PEt$_3$)}$_2$] (**6**) was undertaken, but the instability in the electrolyte medium of the other ones precluded their electrochemical investigation. For comparative purposes and to assist in the identification of the redox waves, the corresponding starting compounds *trans*-[Mo(NCN)$_2$(dppe)$_2$], *trans*-[ReCl(N$_2$)(PMePh$_2$)$_4$] and [Pt$_2$Cl$_4$(PEt$_3$)$_2$] were also studied. The redox potentials (V vs. SCE), measured by CV in 0.2 м [NBu$_4$][BF$_4$]/CH$_2$Cl$_2$, at a Pt disc electrode, are listed in Table 1.

Hence, dinuclear adduct **3** exhibits four single-electron oxidation waves that were assigned on the basis of their potentials to the Re$^{\mathrm{I}}$ → Re$^{\mathrm{II}}$ (wave I), Re$^{\mathrm{II}}$ → Re$^{\mathrm{III}}$ (wave III), Mo$^{\mathrm{IV}}$ → Mo$^{\mathrm{V}}$ (wave II) and Mo$^{\mathrm{V}}$ → Mo$^{\mathrm{VI}}$ (wave IV) processes. The oxidation potentials for the first ($^{\mathrm{I}}E_{1/2}{}^{\mathrm{ox}}$ = 0.12 V) and third ($^{\mathrm{III}}E_{\mathrm{p}}{}^{\mathrm{ox}}$ = 1.05 V) anodic waves of **3** are significantly lower than those (0.24 and 1.28 V, respectively) for the Re Lewis acid precursor *trans*-[ReCl(N$_2$)(PMePh$_2$)$_4$], thus indicating that in adduct **3** the {Mo(NCN)$_2$(dppe)$_2$} ligand behaves as a stronger electron donor to Re than one PMePh$_2$ in the starting complex.

The other oxidation waves (II and IV) of **3** are believed to be centred at the Mo site, their oxidation potentials ($^{\mathrm{II}}E_{\mathrm{p}}{}^{\mathrm{ox}}$ = 0.79 and $^{\mathrm{IV}}E_{\mathrm{p}}{}^{\mathrm{ox}}$ = 1.35 V, respectively) being close to those (0.71 and 1.34 V, respectively) of Mo$^{\mathrm{IV/V}}$ and Mo$^{\mathrm{V/VI}}$ for *trans*-[Mo(NCN)$_2$(dppe)$_2$]. The slightly higher value of the Mo$^{\mathrm{IV/V}}$ oxidation wave in adduct **3**, relative to that of the free Mo$^{\mathrm{IV}}$ complex, can possibly be accounted for by the electron release from the Mo centre to the Re site upon coordination. This can also explain the higher (less cathodic) Mo$^{\mathrm{IV/III}}$ reduction potential of **3** ($^{\mathrm{I}}E_{\mathrm{p}}{}^{\mathrm{red}}$ = –1.66 V) in comparison with that (–1.82 V) of the free Mo$^{\mathrm{IV}}$ complex.

Adduct **6** displays one single-electron reversible oxidation ($^{\mathrm{I}}E_{1/2}{}^{\mathrm{ox}}$ = 0.94 V) and one single-electron reversible reduction ($^{\mathrm{I}}E_{1/2}{}^{\mathrm{ox}}$ = –1. 17 V) by CV (Figure 1). The former wave concerns the Mo$^{\mathrm{IV/V}}$ oxidation (no oxidation was detected for the parent Pt$^{\mathrm{II}}$ complex), which undergoes a higher anodic shift of the oxidation potential ($\Delta E_{1/2}{}^{\mathrm{ox}}$ = 0.23 V) upon coordination to Pt$^{\mathrm{II}}$ (in **6**) than to Re$^{\mathrm{I}}$ (in **3**). This is consistent with the additive effect of the two {PtCl$_2$(PEt$_3$)} moieties in trinuclear compound **6** and the stronger Lewis acid character of this Pt$^{\mathrm{II}}$ centre in comparison with {ReCl(N$_2$)(PMePh$_2$)$_3$} in **3**. The reduction wave of **6** conceivably is also centred at the Mo$^{\mathrm{IV}}$ site (Mo$^{\mathrm{IV/III}}$ reduction) and the pronounced shift towards a less cathodic potential upon coordination (from –1.82 to –1.17 V) can also be accounted for by the above types of factors.

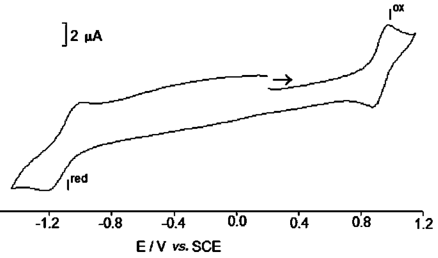


Figure 1. Cyclic voltammogram (starting with the anodic scan) for a solution of [Mo(dppe)$_2${(μ-NCN)PtCl$_2$(PEt$_3$)}$_2$] (**6**) (*c* = 0.98 mм) in 0.2 м [NBu$_4$][BF$_4$]/CH$_2$Cl$_2$, recorded at a scan rate of 0.2 V s^{-1}, at a Pt disc working electrode.

In view of the reversibility of the Mo$^{\mathrm{IV/V}}$ oxidation wave and of the Mo$^{\mathrm{IV/III}}$ reduction wave of **6**, and of the irreversibility of the corresponding waves of **3**, it can be concluded

Table 1. Cyclic voltammetric data[a] for the starting molybdenum, rhenium and platinum compounds and for derived adducts **3** and **6**.

Complex	($^{\mathrm{I}}E_{1/2}{}^{\mathrm{ox}}$)	$^{\mathrm{II}}E_{\mathrm{p}}{}^{\mathrm{ox}}$ ($^{\mathrm{II}}E_{1/2}{}^{\mathrm{ox}}$)	$^{\mathrm{III}}E_{\mathrm{p}}{}^{\mathrm{ox}}$	$^{\mathrm{IV}}E_{\mathrm{p}}{}^{\mathrm{ox}}$	$^{\mathrm{I}}E_{\mathrm{p}}{}^{\mathrm{red}}$ ($^{\mathrm{I}}E_{1/2}{}^{\mathrm{red}}$)	$^{\mathrm{II}}E_{\mathrm{p}}{}^{\mathrm{red}}$
trans-[Mo(NCN)$_2$(dppe)$_2$]	(0.71)	1.34	–	–	–1.82	–
trans-[ReCl(N$_2$)(PMePh$_2$)$_4$]	(0.24)	(1.28)	–	–	–	–
[Mo(NCN)(dppe)$_2$(μ-NCN)ReCl(N$_2$)(PMePh$_2$)$_3$] (**3**)	(0.12) Re$^{\mathrm{I/II}}$	0.79 Mo$^{\mathrm{IV/V}}$	1.05 Re$^{\mathrm{II/III}}$	1.35 Mo$^{\mathrm{V/VI}}$	–1.66 Mo$^{\mathrm{IV/III}}$	–
[Pt$_2$Cl$_4$(PEt$_3$)$_2$]	–	–	–	–	–1.44	–1.68
[Mo(dppe)$_2${(μ-NCN)PtCl$_2$(PEt$_3$)}$_2$] (**6**)	(0.94) Mo$^{\mathrm{IV/V}}$	– –	– –	– –	(–1.17) Mo$^{\mathrm{IV/III}}$	–

[a] In 0.2 м [NBu$_4$][BF$_4$]/CH$_2$Cl$_2$ at a Pt disc electrode (*d* = 0.5 mm) and at a scan rate of 0.2 V s^{-1}. Potentials in V ± 0.02 vs. SCE. Values in brackets correspond to half-wave potentials of reversible waves, whereas the other ones are peak potentials of irreversible waves.

that the electrogenerated Mo^{V}/Pt^{II} and Mo^{III}/Pt^{II} species are more stable in the electrolytic medium than the corresponding Mo^{V}/Re^{II} and Mo^{III}/Re^{I} species derived from **3**.

Conclusions

This work shows that the cyanoimide NCN^{2-} ligand can behave as an effective Lewis base towards a variety of transition metal (M) Lewis acids to yield heterometallic complexes with bridging NCN, which thus acts as a linker or coupler of distinct transition metal cores. Because two cyanamide ligands are present in the starting *trans*-$[Mo(NCN)_2(dppe)_2]$ complex, not only dinuclear but also trinuclear assemblies can be obtained, namely, of the types NCN-*Mo*-NCN-M and M-NCN-*Mo*-NCN-M, in which M pertains to any of the elements of groups 5–8 or 10.

Moreover, the cyanoimide ligands are derived from cyanamide ($N{\equiv}C{-}NH_2$), which thus has been applied to assemble the involved transition-metal units towards building heterometallic frameworks. The synthetic potential of this approach deserves to be further explored for a wider variety of transition-metal Lewis acids and of starting cyanoimide and/or cyanamide complexes.

Cyclic voltammetry allowed the redox properties of some of the heterometallic complexes to be investigated, and the redox potentials of adducts **3** and **6** appear to reflect the net electron donor/acceptor abilities of the metal centres involved, the Pt^{II} site $\{PtCl_2(PEt_3)\}$ behaving as a stronger Lewis acid compared to the Re^{I} metal centre $\{ReCl(N_2)(PMePh_2)_3\}$. However, the instability in the electrolyte medium of the other adducts precluded a reliable electrochemical investigation.

Experimental Section

General: All reactions were carried out under an atmosphere of nitrogen through standard vacuum and inert gas flow techniques. The solvents were dried by standard procedures and freshly distilled before use. The complexes *trans*-$[Mo(NCN)_2(dppe)_2]$,[6,7] $[VCl_3(thf)_3]$,[23a] $[WCl_4(PPh_3)_2]$,[23b] *trans*-$[ReCl(N_2)(PMePh_2)_4]$,[23c] *trans*-$[FeBr(NCC_6H_4NO_2\text{-}4)(depe)_2][BF_4]$,[22] $[Pt_2Cl_4(PEt_3)_2]$[23d] and $[ReOCl_3(PPh_3)_2]$[23e] were prepared according to published methods. C, H and N microanalyses were carried out by the Microanalytical Service of the Instituto Superior Técnico in Lisbon. Infrared spectra were recorded with a Bio-Rad FTIR spectrometer in KBr pellets (4000–400 cm^{-1}; intensity of bands are referred to as s = strong, vs = very strong or br. = broad). ^{1}H, ^{13}C and $^{31}P\{^{1}H\}$ NMR spectra were recorded with a Varian Unity 300 spectrometer at ambient temperature and in CD_2Cl_2 [δ values in ppm relative to $SiMe_4$ (^{1}H and ^{13}C) or $P(OMe)_3$ (^{31}P)]. Abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, qt = quintet, m = multiplet, dt = doublet of triplets, dq = doublet of quartets. Fast-atom bombardment (FAB) mass spectrometric measurements were performed with a Trio 2000 instrument and the positive-ion FAB spectra were obtained by bombarding 3-nitrobenzyl alcohol (NOBA) matrixes of the samples with 8 KeV xenon atoms. Mass calibration for the data acquisition system was achieved by using CsI. The electrochemical experiments were performed with an EG&G PAR 273A potentiostat/galvanostat connected to a computer through a GPIB interface. Cyclic voltammograms were obtained in 0.2 M solutions of $[NBu_4][BF_4]$ in CH_2Cl_2, at a platinum-disc working electrode (0.5 mm diameter) probed by a Luggin capillary connected to a silver wire pseudoreference electrode; a Pt auxiliary electrode was employed. The electrochemical experiments were performed under a nitrogen atmosphere at room temperature, by using an electrochemical cell provided with nitrogen inlet and outlet arms. The potentials of the complexes were measured by CV in the presence of ferrocene as the internal standard, and the redox potential values are normally quoted relative to the SCE by using the $[Fe(\eta^{5}\text{-}C_6H_5)_2]^{0/+}$ ($E_{1/2}^{ox}$ = 0.525 V vs. SCE)[24] redox couple in 0.2 M $[NBu_4][BF_4]$-CH_2Cl_2.

General Procedure for the Preparation of the Complexes: To a CH_2Cl_2 or thf (20 mL) suspension of *trans*-$[Mo(NCN)_2(dppe)_2]$ (0.050 g, 0.051 mmol) at room temperature and under an atmosphere of nitrogen was added the adequate amount of the transition-metal Lewis acid, specifically: $[WCl_4(PPh_3)_2]$ (0.044 g, 0.052 mmol), $[ReOCl_3(PPh_3)_2]$ (0.043 g, 0.052 mmol), *trans*-$[ReCl(N_2)(PMePh_2)_4]$ (0.054 g, 0.051 mmol), *trans*-$[FeBr(NCC_6H_4NO_2)(depe)_2][BF_4]$ (0.040 g, 0.051 mmol), $[VCl_3(thf)_3]$ (0.038 g, 0.102 mmol) or $[Pt_2Cl_4(PPh_3)_2]$ (0.040 g, 0.052 mmol). The suspension, whose colour changed immediately, was left to stir for 3 h, whereafter the solid residue was separated by filtration and then discarded. The filtrate was concentrated under vacuum and *n*-pentane was added (with stirring) to give a solid precipitate of the corresponding adduct, which was separated by filtration, washed with *n*-pentane and dried under vacuum.

***trans*-[Mo(NCN)(dppe)₂(μ-NCN)WCl₄(PPh₃)] (1):** Yield: 0.043 g, 53%. Brown solid. $C_{72}H_{63}Cl_4MoN_4P_5W{\cdot}2.5CH_2Cl_2$ (1730.09): calcd. C 50.5, H 3.9, N 3.2; found C 50.1, H 4.3, N 3.4. IR (KBr): $\tilde{\nu}$ = 2030 [vs, br., $\nu_{as}(N{=}C{=}N)$], 1280 [s, $\nu_{s}(N{=}C{=}N)$ and/or $\nu_{s}(MN)$] cm^{-1}. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.8–6.7 (m, 55 H, C_6H_5, dppe + PPh_3), 3.00 (m, CH_2, dppe) ppm. $^{31}P\{^{1}H\}$ NMR (121.4 MHz, CD_2Cl_2): δ = –95.1 (s, $^{1}J_{P,W}$ = 308.9 Hz, 1 P, PPh_3), –102.7 (s, 4 P, dppe) ppm. MS(FAB+): *m/z* = 1576 $[M + O]^{+\cdot}$, 1541 $[M - Cl + O]^{+\cdot}$, 1118 $[M - 4Cl - PPh_3 - NCN]^{+\cdot}$, 974 $[Mo(NCN)_2(dppe)_2]^{+\cdot}$, 518 $[WCl_2(PPh_3)]^{+\cdot}$, 481 $[WCl(PPh_3)]^{+\cdot}$.

***trans*-[Mo(NCN)(dppe)₂(μ-NCN)ReOCl₃(PPh₃)] (2):** Yield: 0.048 g, 61%. Green solid. $C_{72}H_{63}Cl_3MoN_4OP_5Re{\cdot}1.5CH_2Cl_2$ (1671.07): calcd. C 52.8, H 4.0, N 3.4; found C 52.6, H 4.0, N 3.5. IR (KBr): $\tilde{\nu}$ = 2045 [vs, br., $\nu_{as}(N{=}C{=}N)$], 1279 [s, $\nu_{s}(N{=}C{=}N)$ and/or $\nu_{s}(MN)$], 965 [s, $\nu(Re{=}O)$] cm^{-1}. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.8–6.7 (m, 55 H, C_6H_5), 3.08 (m, 8 H, CH_2) ppm. $^{31}P\{^{1}H\}$ NMR (121.4 MHz, CD_2Cl_2): δ = –102.1 (s, 4 P, dppe), –175.0 (s, 1 P, PPh_3) ppm. MS (FAB+): *m/z* = 1421 $[M - 3Cl - O]^{+}$, 1247 $[M - Cl - PPh_3]^{+}$, 1175 $[M - 3Cl - PPh_3]^{+}$, 1063 $[Re(NCN)_2(dppe)_2]^{+}$, 974 $[Mo(NCN)_2(dppe)_2]^{+\cdot}$, 665 $[Re(NCN)_2(dppe)]^{+}$, 641 $[ReO(NCN)(dppe)]^{+}$.

***trans*-[Mo(NCN)(dppe)₂(μ-NCN)ReCl(N₂)(PMePh₂)₃] (3):** Yield: 0.031 g, 29%. Magenta solid. $C_{93}H_{87}ClMoN_6P_7Re{\cdot}1.5CH_2Cl_2$ (1950.54): calcd. C 53.8, H 4.3, N 4.1; found C 53.8, H 4.4, N 3.8. IR (KBr): $\tilde{\nu}$ = 2042 [vs, $\nu_{as}(N{=}C{=}N)$], 1281 [s, $\nu_{s}(N{=}C{=}N)$ and/or $\nu_{s}(MN)$], 1920 [s, $\nu_{as}(N{=}N)$], 890 [vs, $\nu_{3}(ReO_4)$]. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.8–6.4 (m, 70 H, C_6H_5), 2.72 (t, $1/2|^{2}J_{H,P} + {}^{3}J_{H,P}|$ = 8.5 Hz, 8 H, CH_2), 1.49 (t, $J_{H,P}$ = 3 Hz, 6 H, P_BMePh_2), 1.29 (d, $^{2}J_{H,P}$ = 7.8 Hz, 3 H, P_AMePh_2) ppm. $^{31}P\{^{1}H\}$ NMR (121.4 MHz, CD_2Cl_2): δ = –104.6 (s, 4 P, dppe), –167.5 (d, $^{2}J_{PA,PB}$ = 9.7 Hz, 2 P, P_BMePh_2), –169.0 (t, $^{2}J_{PA,PB}$ = 9.7 Hz, 1 P, P_AMePh_2) ppm. MS (FAB+): *m/z* = 1596 $[M - 2N - PMePh_2]^{+\cdot}$, 1396 $[M - 2N - 2PMePh_2]^{+\cdot}$, 1196 $[M - 2N - 3PMePh_2]^{+\cdot}$, 998 [M –

2N – 2PMePh$_2$ – dppe]$^{+\cdot}$, 974 [Mo(NCN)$_2$(dppe)$_2$]$^{+\cdot}$, 822 [ReCl(PMePh$_2$)$_3$]$^{+\cdot}$, 622 [ReCl(PMePh$_2$)$_2$]$^{+\cdot}$, 422 [ReCl(PMePh$_2$)]$^{+\cdot}$.

***trans*-[Mo(NCN)(dppe)$_2$(µ-NCN)Fe(NCC$_6$H$_4$NO$_2$-4)(depe)$_2$][BF$_4$]Br (4):** Yield: 0.032 g, 35%. Dark-green solid. $C_{81}H_{100}BBrF_4FeMoN_6O_2P_8\cdot 4CH_2Cl_2$ (2095.71): calcd. C 48.8, H 5.2, N 4.0; found C 48.1, H 4.3, N 3.5. IR (KBr): $\tilde{\nu}$ = 2045 [vs, ν_{as}(N=C=N)], 1282 [s, ν_s(N=C=N) and/or ν_s(MN)], 2175 [m, ν(N≡C)], 1581 [m, ν_{as}(NO$_2$)], 1338 [m, ν_s(NO$_2$)], 1160–1000 [vs, br., ν_3(BF$_4$)] cm^{-1}. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ = 8.39 (d, $^3J_{H,H}$ = 7.2 Hz, 2 H, H_{meta} nitrile), 8.30 (d, $^3J_{H,H}$ = 7.2 Hz, 2 H, H_{ortho} nitrile), 8.0–6.8 (m, 40 H, *Ph* dppe), 2.31 (m, 8 H, CH_2 dppe), 2.15 (m, 8 H, CH_2 depe), 1.94 (m, 16 H, CH_2CH$_3$ depe), 1.32 (m, 24 H, CH$_2$CH_3 depe) ppm. ^{31}P{^{1}H} NMR (121.4 MHz, CD$_2$Cl$_2$): δ = –79.8 (s, 4 P, depe), –104.6 (s, 4 P, dppe) ppm. MS (FAB+): *m*/*z* = 1315 [M – depe – NCC$_6$H$_4$NO$_2$ + Br]$^{+\cdot}$, 1236 [M – depe – NCC$_6$H$_4$NO$_2$]$^{+\cdot}$, 974 [Mo(NCN)$_2$(dppe)$_2$]$^{+\cdot}$, 695 [FeBr(NCC$_6$H$_4$NO$_2$)(depe)$_2$]$^{+\cdot}$, 547 [FeBr(depe)$_2$]$^{+\cdot}$, 468 [Fe(depe)$_2$]$^{+\cdot}$, 341 [Fe(depe)]$^+$. MS (FAB–): *m*/*z* = 87 [BF$_4$]$^-$, 79 [Br]$^-$.

[Mo(dppe)$_2${(µ-NCN)VCl$_3$(thf)}$_2$] (5): Yield: 0.043 g, 59%. Brownish green solid. $C_{62}H_{64}Cl_6MoN_4O_2P_4V_2\cdot 1.5CH_2Cl_2$ (1559.03): calcd. C 52.0, H 4.5, N 3.9; found C 51.6, H 4.3, N 4.2. IR (KBr): $\tilde{\nu}$ = 2069 [vs, br., ν_{as}(N=C=N)], 1334 [s, ν_s(N=C=N) and/or ν_s(MN)] cm^{-1}. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, paramagnetic): δ = 8.39 (d, $^3J_{H,H}$ = 7.2 Hz, 2 H, H_{meta} nitrile), 8.30 (d, $^3J_{H,H}$ = 7.2 Hz, 2 H, H_{ortho} nitrile), 7.9–6.7 (m, *Ph* dppe), 3.7 (m, CH_2 thf), 3.0 (m, CH_2 dppe), 2.3 (m, CH_2 thf) ppm. ^{31}P{^{1}H} NMR (121.4 MHz, CD$_2$Cl$_2$): δ = –103.0 (s) ppm. MS (FAB+): *m*/*z* = 1342 [M – 2thf + O + Cl + 3H]$^{+\cdot}$, 1253 [M – 2thf – Cl]$^+$, 1095 [M – VCl$_3$(thf) – thf – Cl]$^+$, 974 [Mo(NCN)$_2$(dppe)$_2$]$^{+\cdot}$.

[Mo(dppe)$_2${(µ-NCN)PtCl$_2$(PEt$_3$)}$_2$] (6): Yield: 0.064 g, 72%. Yellowish solid. $C_{66}H_{78}Cl_4MoN_4P_6Pt_2\cdot 1.5CH_2Cl_2$ (1868.50): calcd. C 45.5, H 4.5, N 3.2; found C 45.0, H 4.3, N 3.2. IR (KBr): $\tilde{\nu}$ = 2090 [vs, ν_{as}(N=C=N)], 1325 [s, ν_s(N=C=N) and/or ν_s(MN)] cm^{-1}. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ = 7.5–7.0 (m, 40 H, *Ph* dppe), 2.89 (t, $J_{H,P}$ = 7.5 Hz, 8 H, CH_2 dppe), 1.91 (dq, $^3J_{H,H}$ = 8.1 Hz, $^2J_{H,P}$ = 10.6 Hz, 12 H, CH_2 monophosphane), 1.24 (dt, $^3J_{H,H}$ = 8.1 Hz, $^3J_{H,P}$ = 16.4 Hz, 18 H, CH_3 monophosphane) ppm. ^{13}C{^{1}H} NMR (75 MHz, CD$_2$Cl$_2$): δ = 133.93 (qt, $J_{C,P}$ = 10 Hz, C_{ipso}, dppe), 133.19 (m, C_{ortho} or C_{meta}, dppe), 130.51 (s, C_{para}, dppe), 129.44 (m, C_{meta} or C_{ortho}, dppe), 122.64 (d, $^3J_{C,P}$ = 22.6 Hz, N*C*N), 28.77 (qt, $J_{C,P}$ = 8.7 Hz, *C*H$_2$, dppe), 14.37 (d, $^1J_{C,P}$ = 41.5 Hz, *C*H$_2$, PEt$_3$), 7.91 (s, *C*H$_3$, PEt$_3$) ppm. ^{31}P{^{1}H} NMR (121.4 MHz, CD$_2$Cl$_2$): δ = –105.4 (s, 4 P, dppe), –144.6 (s, $^1J_{P,Pt}$ = 3659.9 Hz, 2 P, *P*Et$_3$) ppm. MS (FAB+): *m*/*z* = 1599 [M – 4Cl]$^{+\cdot}$, 1439 [M – PtCl$_2$ – Cl]$^+$, 1357 [M – PtCl$_2$(PEt$_3$)]$^{+\cdot}$, 1321 [M – PtCl$_2$(PEt$_3$) – Cl]$^{+\cdot}$, 991 [Pt(dppe)$_2$]$^{+\cdot}$, 974 [Mo(NCN)$_2$(dppe)$_2$]$^{+\cdot}$, 747 [PtCl(PEt$_3$)(dppe)]$^+$, 711 [Pt(PEt$_3$)(dppe)]$^{+\cdot}$.

Supporting Information (see footnote on the first page of this article): Additional figure with simulated and experimental MS (FAB) isotopic pattern for the [Mo(dppe)$_2${(µ-NCN)Pt(PEt$_3$)}$_2$]$^{+\cdot}$ (*m*/*z* = 1599) radical cation derived from **6**.

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