Chemistry of Molybdenum. Part 5.[1] Synthesis, Spectroscopic and Electrochemical Properties of Bis(2-aminocyclopent-1-ene-1-dithiocarboxylato)(arylimido)dihalogenomolybdenum(VI) Complexes‡

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The preparation of a series of arylimido complexes $[Mo(NC_6H_4X\text{-}p)Y_2(acda)_2]$ (Hacda = 2-aminocyclopent-1-ene-1-dithiocarboxylic acid; X = H, Y = F, Cl, or Br; X = Cl or NO_2, Y = Cl) by O/NPh exchange reaction is reported. A novel synthetic route for the generation of arylimidomolybdenum compounds *via* an oxaziridine precursor has been explored. In $[Mo(NPh)Y_2(acda)_2]$ complexes, a systematic shift of the ligand-to-metal charge-transfer band $[S(\pi)\rightarrow Mo(d\pi)]$ to higher energy occurs as the ligand field strength of Y increases. Electrochemical studies (cyclic voltammetry) of these compounds in dimethylformamide reveal the presence of a quasi-Nernstian couple ($E_{\frac{1}{2}}$ *ca.* −0.12 to −0.21 V) due to Mo^{VI}–Mo^{V} electron transfer followed by a Mo^{V}–Mo^{IV} irreversible reduction process ($E_{p,c}$ *ca.* −0.4 V). It is concluded that the imido group is a poor σ-donor ligand compared to the isoelectronic oxo group.

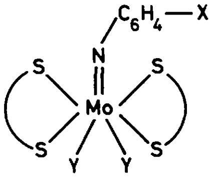
Molybdenum in its higher oxidation states (IV—VI) is predominantly oxophilic.[2] Participation of metal *d* orbitals in π bonding with oxygen provides an adequate explanation for this.[3] The strong tendency of molybdenum to bind oxo ligand(s) is well balanced by its capacity to lose an oxygen atom during oxo-transfer reactions.[4] In fact, excepting nitrogenases, all other biomolybdenum species are oxo-transfer enzymes and catalyse reactions which in effect result in addition or removal of an oxygen atom from the substrate.[4,5] Thus oxygen plays an important role in molybdenum chemistry, particularly in its functions as industrial and biochemical catalysts.

Although it is well recognised that oxo and imido (N–R) ligands are isoelectronic,[6–8] little attention has been paid to the chemistry of imido-molybdenum systems.[8] While the majority of these studies were confined to structural and spectroscopic aspects of compounds containing dithiocarbamates,[6,7,9–11] phosphines,[12,13] and other organic molecules[14–16] as the co-ligands, the electrochemical behaviour of such systems remains, as yet totally unexplored.

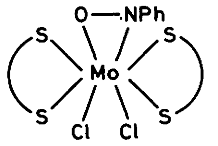
In the last few years, we have been mainly concerned with spectroscopic and electrochemical studies of sulphur-molybdenum systems[1,17–20] designed to test the role of oxygen atom(s) on the overall electron-transfer process. In the present paper we report the synthesis, characterization, and redox properties of some arylimidomolybdenum compounds using 2-aminocyclopent-1-ene-1-dithiocarboxylic acid (Hacda)[18] and its *N*-butyl derivative (Hbacda)[1] as the metal-binding substrates. The results obtained herein have been compared with the corresponding oxo-molybdenum complexes[18] to evaluate the donor abilities of co-ordinated imido compared with the oxo group.

Experimental

All reactions were carried out in redistilled, dry, oxygen-free solvents under dinitrogen atmospheres. Toluene was dried with potassium–benzophenone and distilled under nitrogen before use. The reagents Hacda,[21] Hbacda,[22] N_3Ph,[23] $N_3C_6H_4Cl\text{-}p$,[24] $N_3C_6H_4NO_2\text{-}p$,[25] and PhNHOH[26] were synthesized by known procedures. Freshly distilled N_3Ph (44—45 °C, 4 mmHg) and $N_3C_6H_4Cl\text{-}p$ (32 °C, 1 mmHg) were used. The complexes $[MoOY_2(acda)_2]$ (Y = F, Cl, or Br) were prepared as described previously.[18]



	S⌒S	X	Y
(1)	acda	H	F
(2a)	acda	H	Cl
(2b)	acda	*p*-Cl	Cl
(2c)	acda	*p*-NO_2	Cl
(3)	acda	H	Br
(5)	bacda	H	Cl



(4) S⌒S = bacda

Physical Measurements.—Infrared spectra (4 000—200 cm^{-1}) were recorded as KBr discs on a Perkin-Elmer 783 spectrometer, calibrated with polystyrene film, and u.v.–visible spectra on a Pye-Unicam SP8-150 instrument. Cyclic voltammetry and controlled-potential electrolysis experiments were carried out with a Bioanalytical Systems model CV-27 electroanalytical apparatus. Solutions were *ca.* 10^{-3} mol dm^{-3} with 0.1 mol dm^{-3} tetraethylammonium perchlorate (teap, supporting electrolyte) in dimethylformamide (dmf, 10 cm^3). The solvent (Fluka reagent grade dmf) used in the electrochemical measurements was properly dried and distilled[27] before use. Purified dinitrogen was used to purge the solutions prior to the electrochemical measurements. The electrochemical cell used had a hanging mercury drop (h.m.d.e.) working electrode and a

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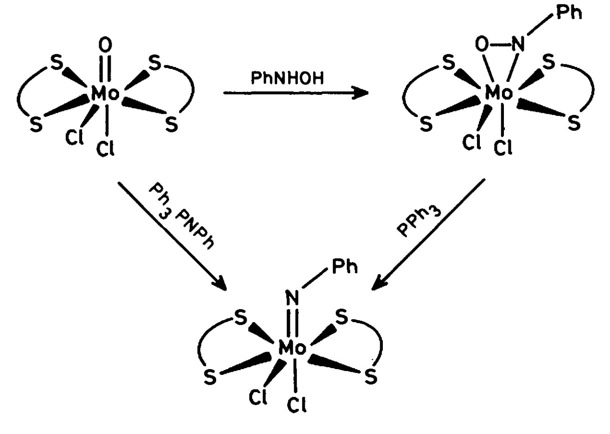
‡ *Non-S.I. unit employed:* mmHg ≈ 133 Pa.

Table 1. Analytical and i.r. data for the complexes

	Analysis[a] (%)					I.r.[c] (cm^{-1})			
Complex	Mo	C	H	N	Y[b]	ν(Mo$\equiv$N)	ν_{asym}(CSS)	ν(Mo$\cdots$S)	ν(Mo–Y)
[Mo(NPh)F_2(acda)$_2$] (**1**)	17.8 (17.7)	39.6 (39.9)	3.8 (3.9)	7.3 (7.8)		955vs	810s	370s	520s
[Mo(NPh)Cl_2(acda)$_2$] (**2a**)	16.8 (16.7)	37.2 (37.6)	3.7 (3.7)	7.0 (7.3)	12.2 (12.3)	960vs	810s	360s	340m
[Mo(NC_6H_4Cl-*p*)Cl_2(acda)$_2$] (**2b**)	15.3 (15.8)	35.2 (35.5)	3.1 (3.3)	6.4 (6.9)	17.3 (17.5)	955vs	810s	355s	320m
[Mo($NC_6H_4NO_2$-*p*)Cl_2(acda)$_2$]·0.5PhMe (**2c**)	14.4 (14.4)	38.0 (38.5)	3.4 (3.6)	8.1 (8.4)	10.2 (10.7)	955vs	810s	355s	320m
[Mo(NPh)Br_2(acda)$_2$] (**3**)	14.9 (14.5)	32.1 (32.6)	3.0 (3.1)	6.1 (6.3)	23.6 (24.1)	955vs	810s	360s	315m
[Mo(η^2-ONPh)Cl_2(bacda)$_2$] (**4**)	13.8 (13.6)	44.5 (44.4)	5.1 (5.3)	5.6 (6.0)	9.9 (10.1)		810s	380m	340m
[Mo(NPh)Cl_2(bacda)$_2$] (**5**)	14.1 (14.0)	44.9 (45.5)	5.3 (5.4)	5.8 (6.1)	10.5 (10.3)	955vs	810s	380m	340m

[a] Calculated values are in parentheses. [b] Y = Halogen. [c] KBr disc.



Scheme.

platinum auxiliary electrode. The oxidation wave for ferrocene in the electroactive solution was used for internal calibration. For controlled-potential electrolysis, a platinum-mesh working electrode was employed. All potentials are referenced to the saturated calomel electrode (s.c.e.) at room temperature and are uncorrected for junction potentials. Elemental analyses (C, H, and N) were determined in this laboratory with a Perkin-Elmer 240C elemental analyser. Molybdenum and halogen contents were estimated by conventional gravimetric methods.

Preparation of Compounds.—Triphenylphosphine arylimide derivatives ($Ph_3P=NC_6H_4X$-*p*; X = H, Cl, or NO_2) were prepared by a literature method.[28] In a typical preparation, triphenylphosphine (0.26 g, 1 mmol) was added to a solution of freshly distilled phenyl azide (0.12 g, 1 mmol) in toluene (10 cm^3). The reaction was allowed to continue until the evolution of nitrogen ceased. The pale yellow solution thus formed was used for subsequent preparation.

[Mo(NPh)F_2(acda)$_2$] (**1**). To a stirred suspension of [MoOF_2(acda)$_2$][18] (0.24 g, 0.5 mmol) in hot (*ca.* 60 °C) toluene (30 cm^3) was added dropwise a solution of Ph_3PNPh (0.35 g, 1 mmol) in toluene (10 cm^3) over a period of 10 min. The reaction mixture was then refluxed for 3 h when a dark green microcrystalline product separated. The compound was filtered off, washed with chloroform (3 × 10 cm^3), and dried *in vacuo* (yield, 80%).

[Mo(NC_6H_4X-*p*)Cl_2(acda)$_2$] (**2a**)—(**2c**). All the chloro complexes were prepared following identical procedures: that for [Mo(NPh)Cl_2(acda)$_2$] (**2a**) is typical. The complex [MoOCl_2(acda)$_2$][18] (0.25 g, 0.5 mmol) was suspended in toluene (30 cm^3) and heated to *ca.* 60 °C. To the stirred suspension was added dropwise a solution of Ph_3PNPh (0.35 g, 1 mmol) in toluene (10 cm^3). The reaction mixture was refluxed for 2.5 h during which time the colour of the solution gradually became dark and a brown product formed. The compound was isolated by filtration, washed with chloroform (4 × 10 cm^3), and dried *in vacuo* (yield, 60—70%).

[Mo(NPh)Br_2(acda)$_2$] (**3**). The procedure was similar to that described for (**1**) except that [MoOBr_2(acda)$_2$][18] was used as starting material (yield, 64%).

[Mo(η^2-ONPh)Cl_2(bacda)$_2$] (**4**). To a stirred CH_2Cl_2 solution (25 cm^3) of [MoOCl_2(bacda)$_2$][1] (0.31 g, 0.5 mmol) was added dropwise PhNHOH (0.07 g, 0.6 mmol) in CH_2Cl_2 (10 cm^3). The resulting deep red solution was stirred at room temperature for 4 h and hexane (20 cm^3) was added to induce precipitation. The orange product was collected by filtration, washed with diethyl ether (4 × 10 cm^3), and dried under vacuum (yield, 42%).

[Mo(NPh)Cl_2(bacda)$_2$] (**5**). To a carefully degassed slurry of (**4**) (0.35 g, 0.5 mmol) in CH_2Cl_2 (25 cm^3) was added dropwise a solution of PPh_3 (0.13 g, 0.5 mmol) in CH_2Cl_2 (5 cm^3).* After refluxing the reaction mixture for 4 h it was cooled to room temperature. The resulting deep red solution was concentrated to *ca.* 5 cm^3 under reduced pressure. Cold diethyl ether (15 cm^3) was then added to precipitate a brown product which was filtered off, washed with diethyl ether (5 × 10 cm^3), and dried *in vacuo* (yield, 55%).

Recrystallizations of compounds (**1**)—(**3**) were not successful because of their insolubility in common organic solvents. Analytical data for the compounds are given in Table 1.

Results and Discussion

Synthesis.—Refluxing [MoOY_2(acda)$_2$] (Y = F, Cl, and Br) with one equivalent of triphenylphosphine arylimide derivatives,

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* Excess of PPh_3 should be avoided since this results in formation of trace quantities of e.s.r.-active, lower valent molybdenum complexes (possibly Mo^V).

Table 2. Summary of electronic spectral[a] and electrochemical[b] data for the compounds

		Mo^{VI}–Mo^{V}			Mo^{V}–Mo^{IV}
Complex	$\lambda_{max.}$/nm	$E_{\frac{1}{2}}$/V[c]	ΔE_p/mV[d]	$i_{p,c}/i_{p,a}$	$E_{p,c}$
(1)	420	−0.12	100	1.05	
(2a)	485	−0.16	110	0.96	−0.43
(2b)	496	−0.17	100	0.92	−0.41
(2c)	505	−0.15	100	0.85	
(3)	508	−0.21	110	0.93	−0.41

[a] Nujol mull. [b] Solvent dmf; supporting electrolyte teap (0.1 mol dm^{-3}); solute concentration *ca.* 10^{-3} mol dm^{-3}. [c] From cyclic voltammogram using a scan rate of 200 mV s^{-1}; $E_{\frac{1}{2}} = 0.5\,(E_{p,c} + E_{p,a})$. [d] $\Delta E_p = E_{p,c} - E_{p,a}$.

$Ph_3P{=}NC_6H_4X$-*p* (X = H, Cl, and NO_2), in toluene under anaerobic conditions led to the exchange of the oxo group by the isoelectronic arylimido ligand (NR), as shown in equation (1). Efforts to obtain the corresponding iodo compound were unsuccessful.

$$[MoOY_2(acda)_2] + Ph_3P{=}NR \longrightarrow [Mo(NR)Y_2(acda)_2] + PPh_3O \quad (1)$$

We have developed yet another interesting route for the preparation of $[Mo(NPh)Cl_2(bacda)_2]$ by abstracting an oxygen atom from the corresponding oxaziridine[29] complex, $[Mo(\eta^2\text{-}ONPh)Cl_2(bacda)_2]$ (Scheme). The rationale for this reaction can be perceived from a concept of the simple effective atomic number rule. In molybdaoxaziridine which is a 16-electron species the relative strain over the three-membered (MoON) ring forces the oxygen atom out when treated with an efficient oxo-abstracting reagent like PPh_3, thus generating a stable 18-electron product, the arylimido compound where imido nitrogen is a four-electron donor.[9] Due to poor solubility characteristics of oxaziridines, this method could not be extended for the preparation of arylimido compounds of Hacda.

Characterization.—The compounds **(1)**—**(3)** are sparingly soluble in common organic solvents except dmf and Me_2SO. They are fairly stable in the solid state. Conductivity measurements in dmf indicate that the complexes are uncharged; upon standing, however, conductivity slowly increases, probably due to halide ion dissociation. This observation can be explained by assuming the molecules to have a seven-co-ordinate geometry around the metal centre as reported for similar dithiocarbamato complexes.[9] Thus $[Mo(NR)Y_2(acda)_2]$ complexes, being 18-electron species, will exert very little *trans* influence[30] on the co-ordinated halide ions.

Infrared Spectra.—Pertinent i.r. bands of the reported complexes are listed in Table 1. Each of the compounds **(1)**—**(3)** contains a single sharp carbon–sulphur stretching vibration at *ca.* 810 cm^{-1} due to ν_{asym}(CSS) with no evidence for splitting, indicating a bidentate, S,S mode of chelation from the ligands as mentioned previously.[1,18,19] The appearance of phenyl-ring vibrations in the region 690—760 cm^{-1} together with a strong band at *ca.* 955 cm^{-1} due to ν(MoN)[31] confirm the presence of the arylimido group in the co-ordination sphere. The compounds $[Mo(NR)Y_2(acda)_2]$ **(1)**—**(3)** also contain a medium intensity band in the range 520—315 cm^{-1} due to ν(Mo–Y) vibrations,[18] the frequency of which changes in the order F > Cl > Br. The i.r. spectrum of the oxaziridine complex **(4)** is almost identical to those of the other molybdenum compounds **(1)**—**(3)**, except for the region 1 000—850 cm^{-1} where lack of a strong band indicates the absence of terminal ν(MoO) or ν(MoN) vibrations. Reappearance of this band at 955 cm^{-1} along with phenyl-ring vibrations indicates the formation of the phenylimido compound **(5)** from the oxaziridine precursor as shown in the Scheme.

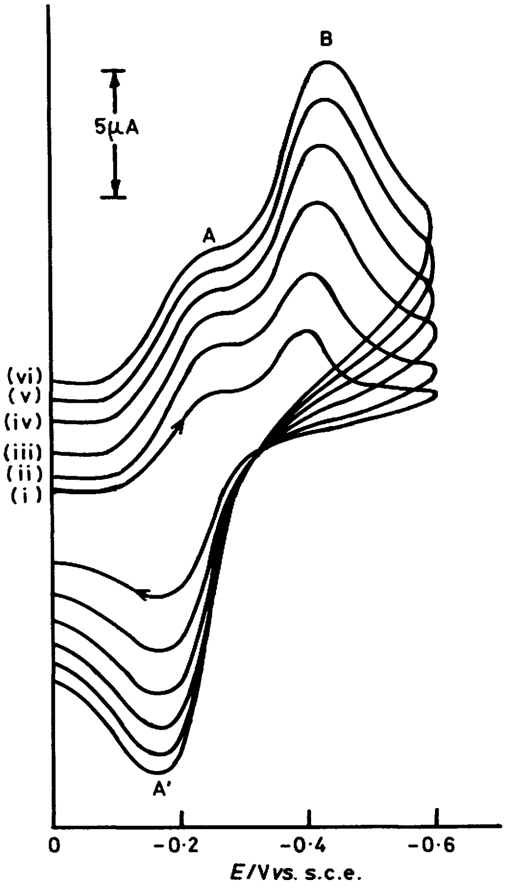

Figure. Cyclic voltammetric traces for $[Mo(NPh)Br_2(acda)_2]$ (*ca.* 1 × 10^{-3} mol dm^{-3}) in 0.1 mol dm^{-3} teap–dmf [scan rates: (i) 100, (ii) 200, (iii) 300, (iv) 400, (v) 500, and (vi) 600 mV s^{-1}]

Electronic Spectra.—A low-energy absorption band in the visible region is observed (Nujol mull) for each of the arylimidomolybdenum compounds reported here (Table 2). By analogy with the spectra of isoelectronic $[MoOY_2(acda)_2]$ (Y = halide ion) compounds,[18] these intense bands are assigned to ligand-to-metal charge transfer (l.m.c.t.) transitions of the type S(π)→Mo(dπ). The π–π* bands characteristic of the dithiocarboxylate ligands[32] occur in the u.v. region. The energy of this l.m.c.t. transition is of particular interest to us as it shows a bathochromic shift on going from fluoro [**(1)**] to bromo [**(3)**] complexes. This is probably due to more effective Mo–Y π-bonding with heavier halogen atoms, which in turn causes lowering of the l.u.m.o. (lowest unoccupied molecular orbital) energy level.

Electrochemistry.—Electrochemical data for the complexes are summarized in Table 2. The cyclic voltammogram (c.v.) of $[Mo(NPh)Br_2(acda)_2]$ in dmf (Figure) reveals the presence of a reversible redox couple (AA′) with $E_{\frac{1}{2}}$ = −0.21 V, followed by an irreversible reduction process (B) at $E_{p,c}$ = −0.41 V. The ligand Hacda is electrode inactive in the potential range studied (+0.5 to −1.8 V). Almost identical c.v.s were obtained for the other complexes, except for **(1)** and **(2c)** in which the wave B was missing. The couple AA′ in all cases displayed quasi-Nernstian

Table 3. Charge-transfer transition energy ($\nu_{\text{l.m.c.t.}}$) and electrochemical potential ($E_{\frac{1}{2}}$) data for [$MoOY_2(acda)_2$] and [$Mo(NPh)Y_2(acda)_2$] complexes

	$\nu_{\text{l.m.c.t.}}$/cm^{-1}		$E_{\frac{1}{2}}$/V	
Compound	Z = O[a]	Z = NPh[b]	Z = O[a]	Z = NPh[b]
[$Mo(Z)F_2(acda)_2$]	23 800	23 800	−0.76	−0.12
[$Mo(Z)Cl_2(acda)_2$]	21 000	20 600	−0.29	−0.16
[$Mo(Z)Br_2(acda)_2$]	20 200	19 700	−0.27	−0.21

[a] Ref. 18. [b] This work.

behaviour, as indicated by the ratio of the peak currents ($i_{p,c}/i_{p,a}$) which remained close to unity (0.95 ± 0.1), the current functions, which varied linearly with the square root of the scan rate v (in the range 100—600 mV s^{-1}). The peak potential separations (ΔE_p) in this potential range varied between 100 and 110 mV, increasing slightly with higher scan rate, indicating again a quasi-Nernstian behaviour involving Mo^{VI}–Mo^{V} one-electron transfer, equation (2). An almost identical value of ΔE_p

$$[Mo^{VI}(NR)Y_2(acad)_2] \xrightleftharpoons{e^-} [Mo^{V}(NR)Y_2(acda)_2]^- \quad (2)$$

(90 mV) is observed for the ferrocenium–ferrocene couple.[33] Constant-potential coulometry performed at potentials more negative compared to $E_{p,c}$ did not give satisfactory results due to overlapping of the two waves (Figure). However, the one-electron nature of each couple (AA′) is established by comparing the observed current height at $E_{p,c}$ to those of the corresponding authentic one-electron reversible reactions,[1] measured under identical experimental conditions.

Coulometric measurements at *ca.* −0.6 V of the irreversible electron-transfer process at −0.41 V did not give meaningful results due to continuous accumulation of coulombs. Here again a metal-centred (Mo^{V}–Mo^{IV}) one-electron transfer process is proposed, equation (3), by comparing the cathodic peak

$$[Mo^{V}(NR)Y_2(acda)_2]^- \xrightarrow{e^-} [Mo^{IV}(NR)Y_2(acda)_2]^{2-} \quad (3)$$

current height at $E_{p,c}$, particularly at higher scan rates, with the corresponding current parameters of couple AA′ using equation (4)[34,35] where $(n_a\alpha)_{\text{irrev.}} = 0.0477/(E_{p,c} - E_{p,c/2})$ (in volts). The

$$n_{\text{irrev.}} = \frac{0.90(i_{p,c})_{\text{irrev.}}}{(i_{p,c})_{\text{rev.}}} \cdot \frac{(n_{\text{rev.}})^{\frac{3}{2}}}{[(n_a\alpha)_{\text{irrev.}}]^{\frac{1}{2}}} \quad (4)$$

lack of anodic response even at a high scan rate (0.6 V s^{-1}) is due to rapid decomposition of the reduced Mo^{IV} species.

A close inspection of Table 2 reveals some interesting trends in the electrochemical results. For a set of three compounds (**1**), (**2a**), and (**3**), where except for the halide ions the remaining ligand environments are the same, the ease of reduction of the metal centre increases with the increase of ligand field strength of the co-ordinated halide ions. On the other hand, when the same halide environment is maintained, (**2a**)—(**2c**), the trend is such that the electron-withdrawing groups attached to the *para* position of the axial NPh phenyl ring shift the $E_{\frac{1}{2}}$ value to a less negative potential. In both the cases the electron-withdrawing groups attached directly or indirectly to the central metal ion tune the reduction potential to a less negative value by increasing the formal positive charge on the metal centre.

Relative Donor Capacity of Oxo and Arylimido Ligands.—At this stage it is appropriate to compare the spectroscopic and electrochemical data of the phenylimido compounds with those of their oxo counterparts (Table 3), as they are expected to provide some insight regarding relative donor abilities of oxo and imido groups. As the energy of an l.m.c.t. excited state is related to the ease with which the metal is reduced and ligand is oxidized, the more easily reduced complex should have the lower l.m.c.t. state. It is immediately apparent from the data presented in Table 3 that the arylimido compounds as a whole undergo Mo^{VI}–Mo^{V} reduction at less negative potentials and consequently have lower l.m.c.t. states compared to their oxo counterparts. The whole situation can be visualized more easily if it is assumed that the oxo group, being a better σ-covalent ligand compared to its isoelectronic arylimido counterparts, will put a great deal of negative charge in the electron-transfer orbital of the metal and thus force the reduction of [$MoOY_2(acda)_2$] compounds to occur at more negative potentials. Our assumption that the oxo group is a better σ donor, *i.e.* an efficient *trans* labiliser,[36] is shown to be valid by the available crystal structure data for the corresponding dithiocarbamato compounds.[9,37] It has been found that the *trans* Mo–Cl distance (2.504 Å)[37] in [$MoOCl_2(S_2CNEt_2)_2$] is greater than that (2.467 Å)[9] in [$Mo(NPh)Cl_2(S_2CNEt_2)_2$].

Conclusions

The oxo–phenylimido exchange reaction is used here for the synthesis of a number of arylimido-molybdenum compounds of the type [$Mo(NC_6H_4X$-*p*$)Y_2(acda)_2$]. Use of an oxaziridine derivative as possible precursor compound for the generation of imido species has been explored. Imido compounds in general have lower l.m.c.t. states and can be reduced [Mo^{VI}–Mo^{V}] at less negative potentials compared to their oxo counterparts, [$MoOY_2(acda)_2$]. The results are explained in terms of a weaker σ-donor ability of the arylimido ligands compared to the oxo group. To our knowledge, this is the first paper dealing with the electrochemical behaviour of imido-molybdenum compounds.

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