Preparation, Structure, and Redox Properties of Isocyanide Complexes of Molybdenum(0) and Tungsten(0)

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The complexes *trans*-[M(CNR)$_2$(dppe)$_2$] (A) (M = Mo or W; R = Me, Bu^t, Ph, C$_6$H$_4$Me-4, C$_6$H$_4$Cl-4, C$_6$H$_3$Cl$_2$-2,6, or C$_6$H$_4$OMe-4; dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) have been prepared. They have low ν(NC) values which are discussed in terms of their electronic structure. The electrochemical properties of the complexes are described and correlations are drawn between their redox potentials and the electronic properties of the isocyanide ligands.

A LARGE variety of isocyanide complexes of the transition metals has been studied in recent years, and particularly the influence of ligation on the reactivity of isocyanides. Thus, when bound to metals in their normal or higher oxidation states, isocyanides release electron density from an essentially lone-pair orbital on carbon and as a consequence become susceptible to attack at carbon by nucleophilic reagents.[1] An induced strengthening of the C–N σ system also occurs, leading to an increase in ν(NC) on co-ordination.[1] In contrast, when bound to low-valent metals, isocyanides act as efficient π acceptors, increasing the electron density within the π* system and causing a decrease in ν(NC) on ligation.[2] Generally, in such complexes the extent of the π interaction is diminished because the isocyanides compete with carbon monoxide or a number of other isocyanide co-ligands.

We were particularly interested in observing the properties of isocyanides on a strongly electron-releasing metal site where such competition is small. Accordingly, we have prepared [equation (1)] a series of complexes, *trans*-[M(CNR)$_2$(dppe)$_2$] (M = Mo or W; R = Me, Bu^t, Ph, C$_6$H$_4$Me-4, C$_6$H$_4$Cl-4, C$_6$H$_3$Cl$_2$-2,6, or

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[1] J. Chatt, R. L. Richards, and G. H. D. Royston, *J.C.S. Dalton*, 1973, 1433 and refs. therein.

[2] L. Malatesta and F. Bonati, 'Isocyanide Complexes of Metals,' Wiley, New York, 1969.

C_6H_4OMe-4; dppe = $Ph_2PCH_2CH_2PPh_2$), where the metal sites are so strongly electron releasing that they activate dinitrogen.[3] Reaction (1) proceeds smoothly to

$$\textit{trans}\text{-}[M(N_2)_2(dppe)_2] + 2RNC \xrightarrow{thf} \textit{trans}\text{-}[M(CNR)_2(dppe)_2](A) + 2N_2 \quad (1)$$

give high yields: analytical data, *etc.* for the complexes prepared are shown in Table 1.

RESULTS AND DISCUSSION

In their i.r. spectra complexes (A) show only one, rather broad, band assigned to N–C stretching; this is consistent with a *trans* configuration, confirmed by *X*-rays for *trans*-$[Mo(CNMe)_2(dppe)_2]$.[4] Complexes (A) are stable to air in the solid state but decompose in chlorinated solvents where they are most soluble. Thus molecular-weight measurements in solution were unreliable, but a parent ion with a principal peak at *m/e* 1 062 (as required for the predominant ^{184}W isotope) was observed in the mass spectrum of *trans*-$[W(CNMe)_2(dppe)_2]$. A similar isotope pattern appeared at *m/e* 1 021 with a corresponding metastable peak at *m/e* 981, indicating that reaction (2) occurs in the spectrometer beam. On the basis of these data and the crystal

$$[W(CNMe)_2(dppe)_2]^+ \longrightarrow [W(CNMe)(dppe)_2]^+ + MeNC \quad (2)$$

structure of (A; M = Mo, R = Me)[4] all the complexes of the series are considered to be monomeric and *trans*.

TABLE 1

Isocyanide complexes of molybdenum and tungsten

Complex [a]	Colour	Yield (%)	M.p.[b] (θ_c/°C)	Analysis (%) [c] C	H	N	$\bar{\nu}$(NC) [d,e] cm^{-1}	$\Delta\bar{\nu}$ [f] cm^{-1}
$[Mo(CNMe)_2(dppe)_2]$	Red	80	272—274	69.0(69.0)	5.8(5.6)	3.0(2.9)	1 862s,br [d] 1 886s [e]	303 279
$[Mo(CNBu^t)_2(dppe)_2]$	Red	90	257	70.1(70.3)	6.5(6.3)	2.8(2.7)	1 915s,br [d] 1 918s [e]	221 217
$[Mo(CNPh)_2(dppe)_2]$	Red	71	277—282	69.8(72.1)	5.7(5.3)	2.4(2.6)	1 853s,br [d] 1 863s [e]	272 260
$[Mo(CNC_6H_4Me\text{-}4)_2(dppe)_2]$	Red	75	277—280	72.5(72.5)	5.6(5.6)	2.5(2.5)	1 860,sbr [d] 1 872s [c]	262 253
$[Mo(CNC_6H_4OMe\text{-}4)_2(dppe)_2]$	Red	62	237—241	71.3(70.5)	5.8(5.4)	2.6(2.4)	1 866s,br [d] 1 873s [e]	262 255
$[Mo(CNC_6H_4Cl\text{-}4)_2(dppe)_2]$ [g]	Red	60	198—208	67.8(67.9)	5.0(4.8)	2.2(2.4)	1 850s,br [d] 1 850s [e]	280 280
$[Mo(CNC_6H_3Cl_2\text{-}2,6)_2(dppe)_2]$	Red	25	223—227	64.0(64.1)	4.6(4.4)	2.3(2.3)	1 840s,br [d] 1 809s [e]	284 315
$[W(CNMe)_2(dppe)_2]$	Deep red	95	270—274	63.5(63.3)	5.3(5.1)	2.7(2.6)	1 834s,br [d] 1 850s [e]	331 315
$[W(CNBu^t)_2(dppe)_2]$	Deep red	81	249—255	64.3(64.9)	6.0(5.8)	2.7(2.4)	1 904s,br [d] 1 904s [e]	231 231
$[W(CNPh)_2(dppe)_2]$	Deep red	78	218—224	65.9(66.6)	5.3(4.9)	2.4(2.4)	1 846s,br [d] 1 845s [e]	278 279
$[W(CNC_6H_4Me\text{-}4)_2(dppe)_2]$	Deep red	71	277—280	67.4(67.2)	5.1(5.1)	2.4(2.3)	1 847s,br [d] 1 856s [e]	279 270
$[W(CNC_6H_4OMe\text{-}4)_2(dppe)_2]$	Deep red	75	247—252	66.2(65.5)	5.7(5.0)	2.4(2.3)	1 850s,br [d] 1 856s [e]	230 268
$[W(CNC_6H_4Cl\text{-}4)_2(dppe)_2]$	Deep red	90	234—237	63.5(63.1)	4.9(4.5)	2.2(2.2)	1 835s,br [d] 1 828s [c]	295 302
$[W(CNC_6H_3Cl_2\text{-}2,6)_2(dppe)_2]$	Deep red	65	277—282	59.2(59.8)	4.4(4.1)	2.0(2.1)	1 788 [d] 1 790 [e]	336 334

s = Strong, br = broad.

[a] *trans* Configuration (see text). [b] In sealed evacuated tubes with decomposition. [c] Calculated values are given in parentheses. [d] KBr disc. [e] thf solution. [f] $\Delta\bar{\nu} = [\bar{\nu}(NC)$ (free isocyanide) $- \bar{\nu}(NC)$ (ligating isocyanide)]. [g] Cl, 5.6(6.1%).

The values of $\bar{\nu}$(NC) for complexes (A) (Table 1) are very low relative to those of free isocyanides and close to the range of bridging isocyanides (*ca.* 1 750—1 800 cm^{-1}) which have[5] CNC bond angles of *ca.* 135°. The terminal methyl isocyanide ligands of (A; M = Mo, R = Me)[4] have CNC bond angles of 156°. The cause of this bending may be steric but is more probably electronic because the very low $\bar{\nu}$(NC) values do not change significantly when the solid is dissolved in tetrahydrofuran (thf) (Table 1) and these ligating isocyanides readily protonate at their nitrogen atoms.[4] A similar but more pronounced bending has been observed in $[Ru(CNBu^t)_4(PPh_3)]$ [CNC angle 130(2)°] and is also attributed to an electronic effect.[6]

The electronic structure of these complexes may be represented as a combination of the canonical forms (a) and (b), with a large contribution from (b). This would

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[3] J. Chatt, G. A. Heath, and R. L. Richards, *J.C.S. Dalton*, 1974, 2074 and refs. therein.

[4] J. Chatt, A. J. L. Pombeiro, K. W. Muir, R. L. Richards, G. H. D. Royston, and R. Walker, *J.C.S. Chem. Comm.*, 1975, 708; J. Chatt, A. J .L. Pombeiro, and R. L. Richards, unpublished results.

[5] F. A. Cotton and B. A. Frenz, *Inorg. Chem.*, 1974, **13**, 253 and refs. therein.

[6] G. K. Barker, A. M. R. Galas, M. Green, J. A. K. Howard, F. G. A. Stone, T. W. Turney, A. J. Welch, and P. Woodward, *J.C.S. Chem. Comm.*, 1977, 256.

require a relatively short Mo–C bond distance. In (A; M = Mo, R = Me) the observed distance [2.101(7) Å] is shorter than the estimated [7] Mo–C(*sp*) single-bond distance of 2.32 Å but longer than the Mo–CO distance in, for example, $[Mo(CO)_4(Ph_2PCH_2PPh_2)]$ [8] and $[Mo(CO)_6]$ [9] (2.04 and 2.06 Å respectively). Thus there appears to be some π-bond character in the Mo–CNMe bond, but less than in corresponding Mo–CO bonds, as has been noted in other systems.[7] This approach, while simple, is sufficient for our purpose and is essentially in accord with more sophisticated molecular-orbital (m.o.) approaches based on that of Gimarc.[10] Thus the electron-rich $M(dppe)_2$ site releases electron density into the π-antibonding orbitals of isocyanides so strongly that they attain a ' carbene-like ' character, resulting in a particularly low $\bar{\nu}$(NC) value, a reduced CNC bond angle, and a fairly short Mo–C distance.

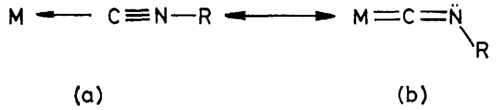

TABLE 2

N.m.r. data for (A; R = Bu^t)

Complex	Nucleus	δ/p.p.m.	Integration [a]	Assignment
trans-$[W(CNBu^t)_2(dppe)_2]$	^1H [b]	2.3—3.2(m)	40(40)	C_6H_5 of dppe
		7.3—7.9(m)	7.8(8)	CH_2 of dppe
		9.38(sbr)	18(18)	$C(CH_3)_3$
	^{31}P [c]	87.97(t)		P of dppe ^1J(WP) 297.9 Hz
trans-$[Mo(CNBu^t)_2(dppe)_2]$	^1H [b]	2.4—3.2(m)	40(40)	C_6H_5 of dppe
		7.4—7.8(m)	8.0(8)	CH_2 of dppe
		9.37(s,br)	18(18)	$C(CH_3)_3$
	^{31}P [c]	67.2(s)		P of dppe

m = Multiplet, s = singlet, br = broad, and t = triplet.

[a] Calculated values are given in parentheses. [b] In C_6D_6 solution, relative to $SiMe_4$. [c] In C_6D_6 solution relative to $P(OMe)_3$.

A similar transfer of metal electron density into antibonding orbitals must occur in the corresponding carbonyl complexes, apparently to a greater extent as judged by Mo–CO bond distances, but there is no diagnostic bond angle to observe at carbonyl oxygen. Infrared spectral measurements are also consistent with the apparently greater π-acceptor capacity of CO ligating the $Mo(dppe)_2$ site, because the fractional lowering of $\bar{\nu}$(CO) ($\Delta\bar{\nu}/\bar{\nu}$, see Table 3) for *trans*-$[Mo(CO)_2(dppe)_2]$ [$\bar{\nu}$(CO) at 1 815 cm^{-1}] [11] is considerably greater (0.221) than the $\Delta\bar{\nu}/\bar{\nu}$ value for (A; M = Mo, R = Me) (0.142, Table 3). Only complexes (A; R = Bu^t) are sufficiently soluble in inert solvents (*e.g.* benzene) for n.m.r. spectral measurements. Their single ^{31}P resonance confirms the *trans* configuration of these complexes (Table 2).

Redox Properties.—The bis(isocyanide) complexes are, as expected, relatively easily oxidised, but difficult to reduce.

The peak potentials obtained from cyclic voltammetry are given in Table 3 and typical voltammetric behaviour is shown in Figure 1 for *trans*-$[Mo(CNBu^t)_2(dppe)_2]$. In general, the alkyl isocyanide complexes gave well defined oxidation waves, whereas the aryl isocyanide complexes showed two well defined and two poorly defined steps. No complex was found to be reducible at potentials between 0 and −2.0 V [*versus* the standard calomel electrode (s.c.e.)] and the free isocyanides were electroinactive between +1.0 and −1.0 V.

TABLE 3

Electrochemical data [a]

R	$E'(1)$	$E_{Pa}(2)$	$E_{Pa}(3)$	$E_{Pa}(4)$	$\frac{\Delta\bar{\nu}^b}{\bar{\nu}}$
(*a*) Molybdenum					
$Bu^{t,\ c}$	−0.623	0.280	0.66		0.098
Me	−0.607	0.140	0.621		0.142
C_6H_4Me-4	−0.450	0.352	*ca.* 0.83	*ca.*0.97	0.116
C_6H_4Cl-4	−0.395	0.393	*ca.* 0.97		0.129
C_6H_4OMe-4	−0.471	0.329	*ca.* 0.82	*ca.* 0.96	0.108
Ph	−0.420	0.418	*ca.* 0.91		0.119
(*b*) Tungsten					
Bu^t	−0.634	0.232	0.532		0.104
Me	−0.598	0.136	0.553		0.151
Me [d]	−1.040	−0.273	0.520		
Me [e]	−1.052	−0.242	0.13	0.48	
C_6H_4Me-4	−0.435	0.324	*ca.* 0.75	*ca.* 0.87	0.124
C_6H_4Cl-4	−0.333	0.388	*ca.* 0.93		0.134
C_6H_4OMe-4	−0.464	0.312	*ca.* 0.73	*ca.* 0.82	0.122
Ph	−0.407	0.387	*ca.* 0.79	*ca.* 0.93	0.126

$E_{Pa}(n)$ and $E_{Pc}(n)$ = anodic and cathodic peak potentials at peak n (n = 1—4).

[a] Measurements in thf–MeOH (80 : 20) (0.1N LiCl). Potentials in volts (± 0.001 V) relative to aqueous potassium chloride calomel electrode. $E'(1)$ is taken as the potential halfway between $E_{Pa}(1)$ and $E_{Pc}(1)$ on a 500 mV scan at 30 mV s^{-1}. [b] Fractional lowering of $\bar{\nu}$(NC); $\Delta\bar{\nu}$ = [$\bar{\nu}$(CN) (free isocyanide) − $\bar{\nu}$(CN) (ligating isocyanide)], $\bar{\nu}$ = $\bar{\nu}$(CN) (free isocyanide), in thf solution. [c] $[Mo(CNBu^t)_2(dppe)_2]^+$ has $E'(1)$ = −0.650 V and $E_{Pc}(2)$ = 0.260 V. [d] Solvent thf–MeCN (0.1N in $Li[ClO_4]$), reference electrode Ag–Ag$[ClO_4]$ (0.1N in MeCN). [e] Solvent thf–MeCN (0.1N in LiCl), reference electrode Ag–Ag$[ClO_4]$ (0.1N in MeCN).

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[7] G. R. Knox, G. A. Sim, J. G. Sime, and D. I. Woodhouse, *J. Organometallic Chem.*, 1974, **74**, C7.,

[8] K. K. Cheung, T. F. Lai, and K. S. Mok, *J. Chem. Soc.* (*A*), 1971, 1644.

[9] S. P. Arnesen and H. M. Seip, *Acta Chem. Scand.*, 1966, **20**, 2711.

[10] B. M. Gimarc, *J. Amer. Chem. Soc.*, 1971, **93**, 815.

[11] L. K. Holden, A. H. Macoby, D. B. Smith, and R. Whyman, *J. Organometallic Chem.*, 1974, **55**, 343.

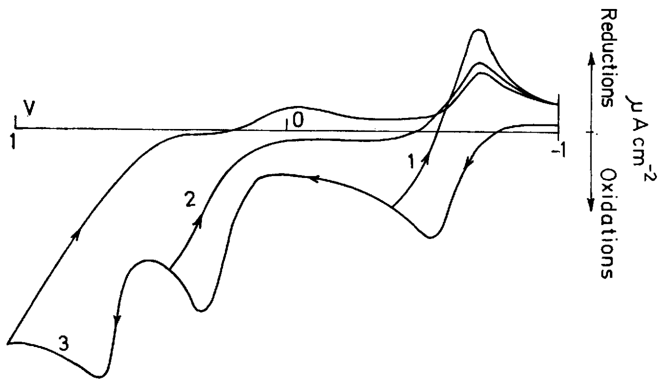
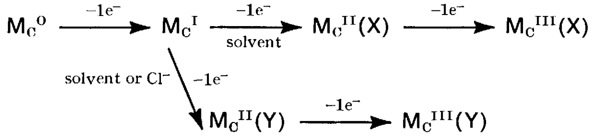


FIGURE 1 Cyclic voltammogram of *trans*-[Mo(CNBu^t)$_2$(dppe)$_2$] in thf–MeOH–LiCl; 1, 2, and 3 = oxidation steps 1, 2, and 3

The primary oxidation step (that at the more negative potential) of both the alkyl and aryl isocyanide complexes met the criteria for a diffusion-controlled one-electron oxidation process (see Experimental section). Controlled-potential oxidation, at potentials 100 mV anodic of the first oxidation peak potential, produced stable metal(I) species. These were characterised by their reduction potentials which coincided with the above oxidation potentials. Their two oxidation waves also closely corresponded to the second and third oxidation steps of the parent metal(0) complexes. The second oxidation step of complexes (A), which occurred between 0.1 and 0.42 V (Table 3 and Figure 1), was totally irreversible. The ratio of the corrected peak current for the first and second steps was very close to unity, indicating that the second process also involved a single electron per molecule.

A controlled-potential electrolysis of (A; M = Mo, R = Me) at 0.35 V (thf–MeOH) produced a stable species which displayed an irreversible oxidation peak at 0.65 V and an irreversible reduction wave on the edge of solvent discharge at −1.6 V. This indicates that the irreversible third oxidation wave observed in the cyclic voltammogram of (A; M = Mo, R = Me) at 0.621 V (Table 3) is due to a stable metal(II) species and not a transient produced at the electrode surface. A comparison of the corrected peak currents showed that this third oxidation step involved a single electron. Complexes (A; R = aryl) showed third and fourth oxidation waves (Table 3), but these were too close to the electrolyte discharge (*ca.* 1.1 V) to be characterised.

The third oxidation wave of (A; M = W, R = Me) is dependent on the electrolyte medium (Table 3) whereas the others show little dependence (after correction for the different reference electrode). Moreover a fourth wave appears when thf–MeCN–LiCl is the electrolyte medium. In this medium, the shift of −0.423 V of the third oxidation step from its value in thf–MeOH–LiCl is close to the corresponding shifts observed for the first two peaks (−0.454 and −0.379 V). This suggests that, in both media, the same tungsten(II) species is initially formed by the irreversible oxidation of [W(CNMe)$_2$(dppe)$_2$]$^+$. Moreover, the fourth oxidation step observed in thf–MeCN–LiCl has a potential (0.48 V) which is close to that of the third oxidation step observed in thf–MeCN–Li[ClO$_4$] (0.52 V); therefore it is due to the oxidation of a second tungsten(II) [rather than a tungsten(III)] species. It appears that during its formation the tungsten(II) isocyanide complex reacts with solvent when Li[ClO$_4$] is the supporting electrolyte, or solvent and/or chloride ion when LiCl is the supporting electrolyte, to give two new species [M$_C$^{II} (X) and M$_C$^{II}(Y)] which can be oxidised. This causes the observed irreversibility of the second oxidation step of (A; M = W, R = Me) and probably a similar process applies to the other complexes of this series (Scheme). No pure products could be isolated from these solutions, but oxidised species have been prepared by halogen or silver(I) oxidation and will be described in a later paper.



M$_C$ = metal complex

SCHEME

Analogous molybdenum and tungsten complexes have similar potentials, those for tungsten being just significantly higher (Table 3). Corresponding *E*(1) values in the analogous series [M(CNR)$_2$(CO)$_4$] (M = Mo or W, R = Pr^i or Bu^t) [12] are also close, but those of the tungsten complexes are now slightly the lower by 0.05 V. Tungsten complexes in their intermediate oxidation states are more readily oxidised than their molybdenum analogues, but from the above data this generalisation does not appear to apply to their metal(0) complexes. Whether they contain good σ donors (phosphines) or good π acceptors (carbon monoxide or isocyanide) their redox potentials are essentially the same.

There is a clear distinction between alkyl and aryl isocyanide complexes, the former being *ca.* 0.15 V easier to oxidise. This accords with the expected greater electron release from alkyl isocyanides and has been noted before.[12,13] Complexes where R = Bu^t are easier to oxidise by one electron than their analogues with R = Me, also expected in view of the greater electron release from the tertiary butyl groups. However, this behaviour does not apply to the second and third oxidation steps, which is not unexpected since these processes are irreversible.

The redox potentials, *E*′(1), corresponding to the first oxidation-reduction process of the aryl derivatives, give a reasonably linear correlation with Hammett σ_p values [14]

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[12] J. A. Connor, M. B. Hall, I. H. Hillier, E. M. Jones, M. K. Lloyd, J. A. McCleverty, G. K. McEwen, and D. G. Orchard, *J.C.S. Dalton*, 1973, 1943.

[13] J. W. Dart, M. K. Lloyd, R. Mason, and J. A. McCleverty, *J.C.S. Dalton*, 1973, 1747.

[14] R. W. Taft, *J. Phys. Chem.*, 1960, **64**, 1805.

(Figure 2), the most electron-withdrawing substituent on the phenyl ring (4-Cl) corresponding to the highest electrode potential. Values of $\Delta\bar{\nu}/\bar{\nu}$ (Table 3) also correlate, but only roughly, with σ_p and $E'(1)$ values. Presumably the C–N stretching frequency, to a first approximation related to the CN bond order, only indirectly reflects the energy of the electrons in the redox orbitals, determined by the effective nuclear charge of the metal (neglecting solvation effects). Nevertheless the energy of the redox orbitals is directly influenced by the electronic effects of the *para* substituents at the isocyanide.

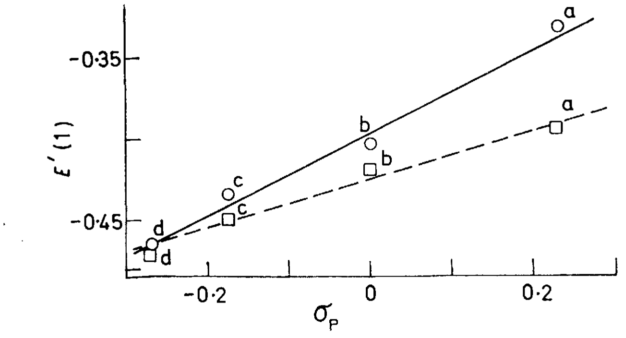

FIGURE 2 Plot of $E'(1)$ against σ_p for *trans*-[M(CNC$_6$H$_4$Y-4)$_2$(dppe)$_2$]. M = W(○) or Mo (□); Y = Cl (a), H (b), Me (c), or OMe (d)

Conclusion.—The electron-rich M(dppe)$_2$ centre is so able to release electron density to ligating isocyanide that the lowering of ν(NC) approaches that found for isocyanides in a bridging position or in some anionic complexes.[15] The low-valent metal complexes (A) are readily and reversibly electrochemically oxidised by one unit and irreversibly by two further units.

EXPERIMENTAL

Experiments with air-sensitive materials were carried out under dinitrogen or argon as appropriate. Gases were manipulated by standard high-vacuum, or nitrogen-flow, techniques. Infrared spectra were determined with a Unicam SP 2000 instrument and n.m.r. measurements were taken with a Jeol P.S. 100 spectrometer. Mass spectra were obtained with an A.E.I. MS9 spectrometer. Conductivities were measured using a Portland electronics conductivity bridge and analyses were by Mr. and Mrs. A. G. Olney of the University of Sussex. Isocyanides [1,2] and *trans*-[M(XY)$_2$(dppe)$_2$] (XY = N$_2$ or CO) [3] complexes were prepared by published methods.

Electrochemical Measurements.—The apparatus and vitreous carbon electrode were as described elsewhere.[16] The solvent used for the bulk of the work was tetrahydrofuran—methanol (80 : 20) which was 0.1N in LiCl. For the experiment where alcohol was excluded, the solvent was thf–MeCN (50 : 50) which contained 0.1N LiCl or Li[ClO$_4$] and the aqueous calomel reference electrode was replaced by an Ag–Ag[ClO$_4$] (0.1N in MeCN) electrode. This reference electrode was separated from the test solution by a salt bridge (0.3N Li[ClO$_4$] in MeCN). All the solutions were *ca.* 10^{-3} mol dm^{-3} in complex and saturated with argon. Redox potentials (defined as in Table 3) were measured at 20 ± 2 °C and carry an error of ± 10 mV.

The first oxidation step (at the more negative potentials) of both the alkyl and the aryl isocyanide complexes matches the criteria for a diffusion-controlled one-electron oxidation process; the separation between the oxidation and reduction peaks was 100 mV and the difference between the oxidation peak potential (E_{pa}) and half-peak potential [$E'(1)$] was 68 mV (in both cases, theoretical values equal 59 mV where n is the number of electrons transferred); [17] also the Malachesky R factor [18] was 5.10 which is close to the theoretical value of 4.92 for a one-electron diffusion-controlled charge-transfer step.

Preparation of Isocyanide Complexes.—Since the method is a general one only one example is given, analytical data, *etc.* for all the complexes prepared being in Table 1.

trans-*Bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*bis*(*methyl isocyanide*)*tungsten*(0), *trans*-[W(CNMe)$_2$(dppe)$_2$]. The complex *trans*-[W(N$_2$)$_2$(dppe)$_2$] (1.04 g, 1.0 mmol) was stirred with methyl isocyanide (0.14 cm^3, 3.4 mmol) in dry thf (30 cm^3) at reflux under dinitrogen for 6 h. Cooling gave the analytically-pure product as red prisms (1.01 g, 0.95 mmol).

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[15] R. D. Adams, *J. Organometallic Chem.*, 1975, **88**, C38.

[16] C. M. Elson, *J.C.S. Dalton*, 1975, 2401.

[17] R. S. Nicholson and I. Shain, *Analyt. Chem.*, 1964, **46**, 706.

[18] P. A. Malachesky, *Analyt. Chem.*, 1969, **41**, 1493.