Mechanism of Alkylation of Alkyldiazenido-complexes of Molybdenum(II) and Tungsten(II): Influence of Metal and Co-ligands on the Nucleophilicity of a Diazenido-group

Wasif Hussain, G. Jeffery Leigh, Hapipah Modh-Ali, and Christopher J. Pickett
AFRC Unit of Nitrogen Fixation, University of Sussex, Brighton BN1 9RQ

The alkylation reaction (1) proceeds *via* an S_N2 process. The nucleophilicity of the diazenido-group is sensitive to the metal, M = Mo or W, and the diphosphine ligands, $R'_2PCH_2CH_2PR'_2$, where

$$trans\text{-}[MBr(N^1N^2Et)(R'_2PCH_2CH_2PR'_2)_2] + MeI \xrightarrow{k_2} trans\text{-}[MBr(N^1N^2MeEt)(R'_2PCH_2CH_2PR'_2)_2]^+ + I^- \quad (1)$$

$R' = p\text{-}X'C_6H_4$ and $X' = CF_3$, Cl, H, Me, or MeO. The second-order rate constants, k_2, for the molybdenum and tungsten analogues are related by the linear-free-energy expression (2); the

$$\ln k_2(W) = 1.12 \ln k_2(Mo) + 1.81 \quad (2)$$

tungsten ethyldiazenido-complexes react about an order of magnitude faster than do their molybdenum counterparts. Substituting CF_3 for MeO groups on the aryl rings of the diphosphine ligands decreases k_2 by about three orders of magnitude for W, somewhat less for Mo. Correlation of k_2 and $E^{0'}(M^{III}/M^{II})$ with the Hammett constant σ shows that the substituent influence on k_2 is predominantly inductive; there is no evidence of through-conjugation from X' to the reaction centre, N^2. The *cis*-PWN^1 unit transmits the influence of X' to the reaction centre more efficiently than does the corresponding Mo unit.

Organodiazenido-complexes of the general type *trans*-$[MX(N^1N^2R)(diphos)_2]$ (M = Mo or W, R = alkyl; X = Br or I, diphos = $Et_2PCH_2CH_2PEt_2$ or $R'_2PCH_2CH_2PR'_2$, R' = aryl) react in tetrahydrofuran (thf) with alkyl bromides or iodides, R″X, to give dialkylhydrazido(2−) derivatives, reaction (1).[1,2] In this reaction M' represents a generalised

$$[M'Br(N^1N^2R)] \xrightarrow[-X^-]{R''X} [M'Br(N^1N^2RR'')]^+ \quad (1)$$

square-planar $M(diphos)_2$ core. This paper is concerned with the mechanism of the alkylation reaction and with the influence which the metal (Mo or W) and the diphosphine co-ligands exert on reactivity.

In a preliminary communication[3] we reported that the alkylation involves a rate-determining bimolecular nucleophilic attack by N^2 on the α-carbon of the alkyl halide, *i.e.* an S_N2 process. Here we present in detail the evidence which supports this conclusion.

Several of the diazenido-complexes used in this study are new, and their properties are described below.

Results and Discussion

Preparation and Properties of the Alkyldiazenido-complexes.—The complexes used in this study were prepared by a general procedure which we have reported earlier.[1,2] Table 1 gives analytical and spectroscopic data for the new compounds.

Each diazenido complex shows a characteristic band in the region 1 500—1 550 cm^{-1} of its i.r. spectra;[1,2] this is assigned to v(N=N). The *trans* stereochemistry of the new compounds is evident from their $^{31}P\text{-}\{^1H\}$ n.m.r. spectra which show a singlet resonance. The ^1H n.m.r. spectra exhibit appropriate aromatic and alkyl resonances which integrate in the correct ratios.

It is noteworthy that the ^{31}P chemical shifts of corresponding Mo and W diazenido-complexes differ by *ca.* 12 p.p.m. A difference of *ca.* 20 p.p.m. is observed between Mo and W complexes in the series *trans*-$[M(N_2)_2(diphos)_2]$:[4] J_{WP} is *ca.* 295 Hz in the tungsten diazenido-series and *ca.* 320 Hz in the (parent) dinitrogen complexes.[4] There is no obvious correlation between ^{31}P chemical shifts and properties of the diphosphine ligands.[4]

Cyclic voltammetry of the diazenido-complexes in tetrahydrofuran (thf)–0.2 mol dm^{-3} $[NBu_4][BF_4]$ at a platinum or vitreous carbon electrode shows that each undergoes a diffusion-controlled reversible one-electron oxidation, reaction (2). Table 2 lists $E^{0'}$ data for the primary oxidation and also peak potential data, E_p^{ox}, for an irreversible secondary oxidation which is observed at more positive potentials. At potentials close to the background limit of the electrolyte, an ill defined reduction process is observed. The variation of $E^{0'}$ with structure and reactivity is discussed below.

$$[M'Br(NNR)] \underset{+e}{\overset{-e}{\rightleftharpoons}}_{E^{0'}} [M'Br(NNR)]^+ \xrightarrow[E_p^{ox}]{-e} \underset{\text{unstable}}{\{[M'Br(NNR)]^{2+}\}} \quad (2)$$

The Mechanism of Alkylation.—As discussed above, each complex undergoes a reversible one-electron oxidation in a thf–electrolyte, reaction (2). We have taken advantage of this to monitor rates of reaction of the diazenido-complexes with alkyl halides:[5] the cyclic voltammetric peak currents, i_p^{ox}, are directly proportional to the concentration of the complex.

Figure 1 shows a typical plot of $\log_e i_p^{ox}$ *versus* time, *t*. The data were obtained under pseudo-first-order conditions, [MeI] ≫ [complex], at 24.5 °C. The plot is linear and this shows that the rate of reaction has a first-order dependence on [complex]. Apparent rate constants, k_{app}, were estimated from

Table 1. Physical data for the ethyldiazenido-complexes, *trans*-$[MBr(N_2Et)\{(p\text{-}X'C_6H_4)_2PCH_2CH_2P(C_6H_4X'\text{-}p)_2\}_2]$

Compound		M.p.		Analysis[b]			$^{31}P\text{-}\{^1H\}$ N.m.r.[c]	^1H N.m.r.[d]
M	X′	(°C)	ν(N=N)[a]/cm^{-1}	C	H	N	(δ/p.p.m.)	(δ/p.p.m.)
Mo	CF_3	205[e]	1 515—1 560s,br	47.1 (47.3)	3.55 (2.90)	1.30 (1.80)	−86.00	0.09—0.07 (t, *3*,NCH_2CH_3), 1.99—1.55 (q, *2*, NCH_2CH_3), 3.48—2.14 (br, s, *8*, PCH_2CH_2P), 7.33—7.06 (m, *32*, C_6H_4) $[C_6D_6]$
Mo	Cl	155	1 515—1 560s,br	49.9 (49.7)	3.75 (3.45)	1.85 (2.15)	−86.54	0.42—0.24 (t, *3*, NCH_2CH_3), 2.36—2.12 (q, *2*, NCH_2CH_3), 2.56—2.36 (br, s, *8*, PCH_2CH_2P), 7.28—7.0 (m, *32*, C_6H_4) $[C_6D_6]$
Mo	H	205	1 505—1 555s,br	62.6 (63.0)	5.55 (5.20)	2.70 (2.70)	−85.26	0.18—0.13 (t, *3*, NCH_2CH_3), 1.82—1.79 (q, *2*, NCH_2CH_3), 2.48—2.55 (br, d, *8*, PCH_2CH_2P), 7.40—7.04 (m, *40*, C_6H_4) $[CD_2Cl_2]$
Mo	Me	129	1 500—1 540s,br	64.9 (65.2)	6.20 (6.10)	2.25 (2.45)	−88.80	0.31—0.20 (t, *3*, NCH_2CH_3), 2.27—2.65 (q, *2*, NCH_2CH_3), 2.67—2.27 (br, s, *8*, PCH_2CH_2P), 7.36—6.57 (m, *32*, C_6H_4), 1.82 (s, *24*, CH_3) $[C_6D_6]$
Mo	OMe	102	1 500—1 535s,br	57.8 (58.6)	5.75 (5.70)	2.20 (2.20)	−87.47	0.59—0.43 (t, *3*, NCH_2CH_3), 2.43—2.35 (q, *2*, NCH_2CH_3), 2.78—2.47 (br, s, *8*, PCH_2CH_2P), 7.80—6.40 (m, *32*, C_6H_4), 3.30 (s, *24*, OCH_3) $[C_6D_6]$
W	CF_3	215	1 500—1 530s,br	44.8 (44.8)	3.05 (2.75)	1.45 (1.70)	−102.04 (J_{WP} 295.41)	0.12—0.00 (t, *3*, NCH_2CH_3), 2.37—2.63 (q, *2*, NCH_2CH_3), 2.44—1.74 (br, s, *8*, PCH_2CH_2P), 7.25—7.06 (m, *32*, C_6H_4) $[C_6D_6]$
W	Cl	171	1 505—1 530s,br	47.6 (46.6)	3.60 (3.25)	2.05 (2.00)	−96.48 (J_{WP} 299.76)	0.41—0.25 (t, *3*, NCH_2CH_3), 2.89—2.49 (m, *10*, NCH_2CH_3 overlap with PCH_2CH_2P), 7.42—7.67 (m, *32*, C_6H_4) $[CD_2Cl_2]$
W	H	210[e]	1 495—1 535s,br	58.0 (58.0)	5.10 (4.80)	2.40 (2.50)	−101.32 (J_{WP} 297.90)	0.61—0.45 (t, *3*, NCH_2CH_3), 2.67—2.26 (q, *2*, NCH_2CH_3), 2.89—2.26 (br, s, *8*, PCH_2CH_2P), 7.72—6.91 (m, *32*, C_6H_4) $[C_6D_6]$
W	Me	234	1 495—1 535s,br	60.4 (60.6)	5.75 (5.65)	2.05 (2.30)	−102.73 (J_{WP} 295.71)	0.30—0.15 (t, *3*, NCH_2CH_3), 2.54—2.31 (q, *2*, NCH_2CH_3), 2.64—1.20 (br, s, *8*, PCH_2CH_2P), 7.41—6.46 (m, *32*, C_6H_4), 1.70 (s, *24*, CH_3) $[C_6D_6]$
W	OMe	129	1 495—1 530s,br	54.8 (54.8)	5.00 (5.10)	1.75 (2.05)	−103.93 (J_{WP} 298.01)	0.66—0.50 (t, *3*, NCH_2CH_3), 3.03—2.90 (q, *2*, NCH_2CH_3), 3.03—2.73 (br, s, *8*, PCH_2CH_2P), 7.86—6.50 (m, *32*, C_6H_4), 3.24 (s, *24*, OCH_3) $[C_6D_6]$

[a] KBr discs. [b] Calculated values in parentheses. Analyses were performed by Mrs. G. Olney of the University of Sussex. [c] In benzene with trimethyl phosphite as external standard; *J* values in Hz. [d] Data in parentheses indicate multiplicity, *relative intensity*, and assignment; solvent is given in square brackets. [e] With decomposition.

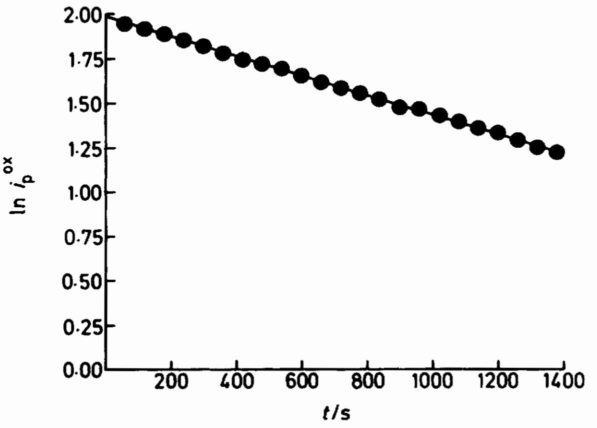


Figure 1. Plot of $\ln i_p^{ox}$ *versus* time, *t* for the reaction of *trans*-$[WBr(N_2Et)\{(p\text{-}MeC_6H_4)_2PCH_2CH_2P(C_6H_4Me\text{-}p)_2\}_2]$ (3 mmol dm^{-3}) with MeI (97 mmol dm^{-3}), in thf–0.2 mol dm^{-3} $[NBu_4][BF_4]$ at 24.5 °C

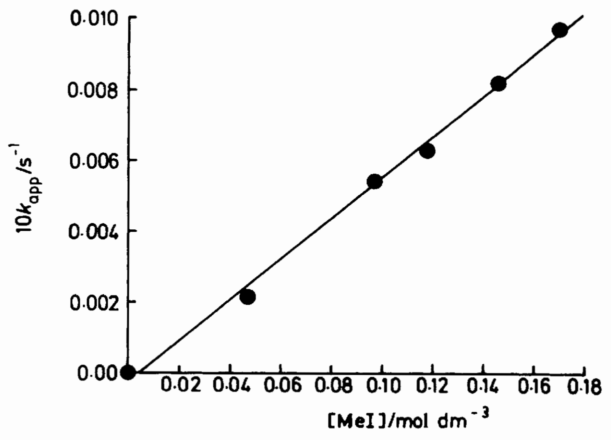


Figure 2. Plot of k_{app} for reaction of *trans*-$[WBr(N_2Et)\{(p\text{-}MeC_6H_4)_2PCH_2CH_2P(C_6H_4Me\text{-}p)_2\}_2]$ with MeI against concentration of MeI at 24.5 °C in thf–0.2 mol dm^{-3} $[NBu_4][BF_4]$

Table 2. Redox and kinetic data for the ethyldiazenido-complexes *trans*-$[WBr(N_2Et)\{(p\text{-}X'C_6H_4)_2PCH_2CH_2P(C_6H_4X'\text{-}p)_2\}_2]$

Complex			
M	X′	$E^{0'a}$/V	$10^5k_2{}^b$/dm^3 mol^{-1} s^{-1}
Mo	CF_3	0.39 (1.55)	0.284
Mo	Cl	0.29 (1.27)	0.526
Mo	H	0.11 (0.99)	8.19
Mo	Me	0.02 (0.90)	67.0
Mo	OMe	−0.05 (0.87)	82.2
W	CF_3	0.38 (1.24)	1.30
W	Cl	0.21 (1.02)	3.43
W	H	0.05 (0.94)	66.3
W	Me	−0.04 (0.81)	578
W	OMe	−0.10 (0.78)	997

[a] Formal potential for reversible one-electron oxidation of complex at Pt electrode in thf–0.2 mol dm^{-3} $[NBu_4][BF_4]$ *versus* s.c.e. The ferrocenium–ferrocene couple is observed at 0.54 V in this system. Values in parentheses are the peak potentials for a secondary irreversible process. [b] Second-order rate constants for the alkylation reaction (1) at 24.5 °C.

the slopes of such plots, at various concentrations of MeI, for each diazenido-complex.

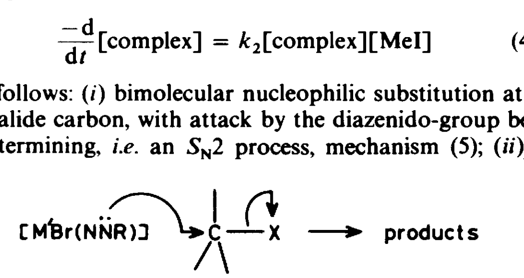
Figure 2 shows a typical plot of k_{app} *versus* [MeI]; the linear dependence of k_{app} on [MeI] shows that the rate of reaction also has a first-order dependence on the alkyl halide concentration. The slopes of such plots provide the second-order rate constants, k_2, for the secondary alkylation reaction, (3); these are listed in Table 2.

$$R''X + [M'Br(NNR)] \xrightarrow{k_2} [M'Br(NNRR'')]^+ + X^- \quad (3)$$

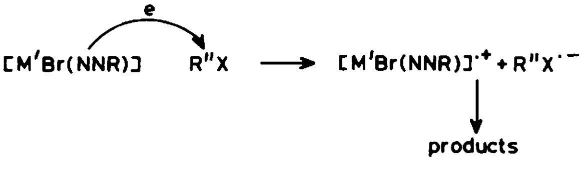
The rate law governing the disappearance of diazenido-complex in the alkylation reaction is represented by equation (4). Two mechanisms which are consistent with this rate law

$$\frac{-d}{dt}[\text{complex}] = k_2[\text{complex}][\text{MeI}] \quad (4)$$

are as follows: (*i*) bimolecular nucleophilic substitution at the alkyl halide carbon, with attack by the diazenido-group being rate-determining, *i.e.* an S_N2 process, mechanism (5); (*ii*) bimolecular single-electron transfer as the rate-limiting step followed by fast attack of the alkyl radical on N^2 [see reaction (1)] in the conjugate M^{III} species, mechanism (6), a single-electron transfer (s.e.t.) pathway. We exclude the operation of the s.e.t. pathway on the basis of the following experimental evidence.



(5)



(6)

The oxidation potentials $E^{0'}$ of the diazenido-complexes are considerably positive of potentials necessary for the reduction of alkyl halides by s.e.t. at significant rates. *trans*-$[MoCl_2(Ph_2PCH_2CH_2PPh_2)_2]$ oxidises reversibly in a one-electron process to give a stable Mo^{III} cation; $E^{0'}$ for this reaction is −0.05 V *versus* a saturated calomel electrode (s.c.e.), a value close to that of the *trans*-$[MoBr(N_2Et)\{(p\text{-}MeOC_6H_4)_2PCH_2CH_2P(C_6H_4MeO\text{-}p)_2\}_2]^{+/0}$ couple.[6] The dichloride does not react with MeI in thf at a measurable rate.

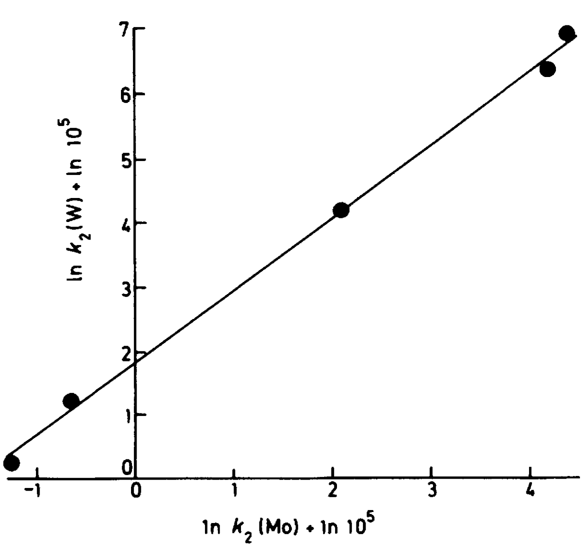


Figure 3. Correlation of ln k_2(W) with ln k_2(Mo)

In the presence of nitrosodurene (2,3,5,6-tetramethylnitrosobenzene) as an alkyl radical trap, e.s.r. spectroscopy showed no evidence for the formation of radicals in the reaction between *trans*-$[MoBr(N_2Et)(Ph_2PCH_2CH_2PPh_2)_2]$ and MeI, neither was the e.s.r.-active complex *trans*-$[Mo^{III}Br(N_2Et)(Ph_2PCH_2CH_2PPh_2)_2]^+$ detected, *cf.* mechanism (6).

The rate of reaction of *trans*-$[WBr(N_2Me)(Ph_2PCH_2CH_2PPh_2)_2]$ with MeI is *ca.* 38 times as fast as is its corresponding reaction with EtI. This is typical of S_N2 reactions, Table 2.[7]

The reaction between *trans*-$[WBr(N_2Me)(Ph_2PCH_2CH_2PPh_2)_2]$ and optically active 2-bromobutane gives the optically active dialkylhydrazido(2−) product, again consistent with the S_N2 reaction pathway; optical yields were not measured.

Taken together, these results are concordant with a classical S_N2 reaction, (5). In the related diazenido-complexes which have had their structure determined by *X*-ray crystallography the NNR bond angle is found to be near 120°.[8] This is indicative of sp^2 hybridisation at N^2 and consistent with alkylation involving the stereochemical lone pair of electrons at this centre.

Influence of the Metal Centre, M = Mo *or* W.—The metal centre exerts an influence on the nucleophilicity of the diazenido-group. Tungsten ethyldiazenido-complexes react with MeI faster than do their molybdenum counterparts, thus $k_{relative}$, the ratio $k_2(W)/k_2(Mo)$, spans the range 4.6—12.1 at 24.5 °C, Table 2.

There is a strict linear-free-energy relationship between $\ln k_2(W)$ and $\ln k_2(Mo)$ as is shown by the plot in Figure 3. The correlation coefficient of the plot is 0.998 and the relationship has the form in equation (7). Because the constant dominates, we can approximate this relationship to equation (8). Using the general expression (9) (h = Planck's constant,

$$\ln k_2(W) = 1.12 \ln k_2(Mo) + 1.81 \quad (7)$$

$$\ln k_{relative} \simeq 2 \quad (8)$$

$$-\Delta G^{\ddagger} = RT \ln k + RT \ln (h/k'T) \quad (9)$$

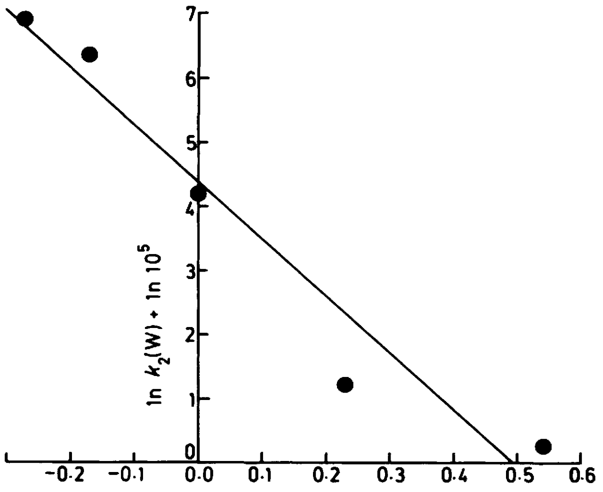


Figure 4. Correlation of ln k_2(W) with the Hammett constant, σ_p

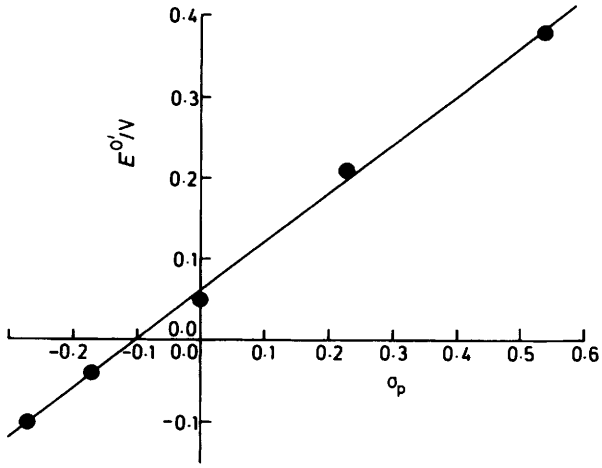


Figure 5. Plot of $E^{0'}$ for the tungsten series of ethyldiazenido-complexes *versus* the Hammett constant, σ_p. Potentials are relative to s.c.e. in thf–0.2 mol dm^{-3} [NBu$_4$][BF$_4$]

k' = Boltzmann's constant) for free energies of activation and the approximation (8) gives $|\Delta G^{\ddagger}(\text{Mo}) - \Delta G^{\ddagger}(\text{W})|$ = *ca.* 5 kJ mol^{-1}.

The oxidation potentials of the tungsten and the molybdenum ethyldiazenido-complexes differ by between 10 and 70 mV, the tungsten complexes being easier to oxidise. This corresponds to $|\Delta G^0(\text{Mo}^{\text{III}}/\text{Mo}^{\text{II}}) - \Delta G^0(\text{W}^{\text{III}}/\text{W}^{\text{II}})|$ being between 1 and 7 kJ mol^{-1}, the same order of magnitude as the activation energy difference.

Nucleophilicity frequently parallels basicity: we do not have data relating to the base strengths of diazenido-ligands, although it has been shown that nitrido and dinitrogen ligands bound to tungsten are considerably more basic than when bound to molybdenum.[9,10]

Influence of the Diphosphine Ligands.—Whilst rates of alkylation of the tungsten ethyldiazenido-complexes are no more than about an order of magnitude faster than those of their molybdenum analogues, variation in reaction rates as a consequence of changing the nature of the diphosphine ligands spans two or three orders of magnitude; electron-withdrawing *para*-substituents on the aryl groups of the diphosphine ligands decrease k_2, electron-donating substituents enhance it, Table 2.

The substituent effect on k_2 is more pronounced when the metal centre is tungsten than when it is molybdenum, *i.e.* tungsten is more efficient in transmitting the electronic influence of the peripheral substituents to N^2.

The electronic influence of the substituents on N^2 is essentially inductive. Figure 4 shows a plot of $\log_{10} k_2$(W) *versus* the Hammett constant, σ_p. Although the relationship is not strictly linear (correlation coefficient 0.97) the dominant trend is clear: the poor correlation of $\log_{10} k_2$(W) with σ^+ (correlation coefficient 0.92) is consistent with little through-conjugation between the aryl substituents and the reaction centre, the lone pair of electrons on the sp^2-hybridised N^2.

The reaction constant, ρ, for the alkylation of the tungsten series is *ca.* −0.6 (*per aryl substituent*). This value is really quite large when one considers that the electronic influence of the aryl substituents operates through the three-atom assembly *cis*-PWN: it attests to the efficiency of this unit in transmitting the effect of the peripheral substituents.

We can obtain a measure of the influence of the aryl substituents on the metal centre 'alone' by consideration of the variation in $E^{0'}$, Table 2: $E^{0'}$ reflects the ease of removing an electron from the redox orbital of the closed-shell metal centre. Figure 5 shows a plot of $E^{0'}$ *versus* the Hammett σ constant for the tungsten series of ethyldiazenido-complexes. The plot is linear (correlation coefficient 0.999) and, as would be expected, electron-donating substituents shift $E^{0'}$ to less positive values. The linear correlation of $E^{0'}$ with σ shows that there is no through-conjugation from substituent to the redox orbital. The inductive influence of the aryl substituents on the $E^{0'}$ values in the ethyldiazenido-series parallels that observed earlier for the parent dinitrogen complexes.[4]

The reaction constant, ρ, is readily determined from the gradient of Figure 5 using the relationship (10). Its value of

$$\frac{1}{8}\mathrm{d}E^{0'}/\mathrm{d}\sigma = -2.303\frac{RT}{F}\cdot\rho = -0.59\rho \qquad (10)$$

−1.25 compares with *ca.* −0.6 for the alkylation at N^2. Whilst the former value relates to ground-state energy changes at W and the latter to activation energy changes at N^2, both pertain to reactions involving an overall change of charge. That activation energies respond to variation in the aryl substituents at nearly half the rate (ρ) of the ground-state free energy emphasises the efficiency with which the substituent influence is transmitted to the sp^2-hybridised reaction centre.

The molybdenum series of ethyldiazenido-complexes show a parallel behaviour to those of tungsten in their correlation of k_2 and $E^{0'}$ with σ.

Conclusions

We summarise our conclusions with respect to the alkylation as follows.

(*i*) The mechanism of alkylation of the diazenido-complexes involves a rate-limiting bimolecular nucleophilic substitution at the alkyl halide carbon by a lone pair of electrons on the sp^2-hybridised terminal nitrogen atom of the diazenido-ligand.

(*ii*) The nucleophilicity of the diazenido-group is greater when bound to tungsten than when bound to molybdenum in otherwise analogous complexes.

(*iii*) Substituents on the aryldiphosphine ligands strongly influence the rate of alkylation: the second-order rate constant, k_2, spans nearly three orders of magnitude on tungsten, less on molybdenum.

(*iv*) The influence of the aryl substituents is primarily inductive; through-conjugation between the substituent and the reaction centre is not evident.

(*v*) The unit *cis*-PMN is an efficient transmitter of substituent influence; transmission is more effective when M = W than when M = Mo.

Experimental

General.—All manipulations were performed under an atmosphere of dry dinitrogen using Schlenk apparatus. Solvents were distilled from an appropriate drying agent immediately before use.

Synthesis of Complexes.—The preparation of the diazenido-complexes *trans*-$[MBr(N_2Et)\{(p\text{-}X'C_6H_4)_2PCH_2CH_2P(C_6H_4X'\text{-}p)_2\}_2]$ (M = Mo or W, X = MeO, Me, Cl, or CF_3) from the compounds *trans*-$[M(N_2)_2\{(p\text{-}X'C_6H_4)_2PCH_2CH_2P(C_6H_4X'\text{-}p)_2\}_2]$ and EtBr follows the general procedure described earlier for the unsubstituted compounds (X' = H).[1,2] Yields of the recrystallised compounds were in the range 20—40% and were not optimised. Analytical, spectroscopic, and melting point data are given in Table 1.

Instrumentation.—Infrared spectra were recorded in KBr discs using a Perkin-Elmer 577 spectrometer. Hydrogen-1 and ^{31}P n.m.r. spectra were recorded on JEOL PS100 and FX90Q spectrometers. Melting points were obtained under dinitrogen using an electrothermal melting point apparatus and are uncorrected.

Electrochemical measurements were made using an EG and G polarographic analyser (PAR 174A) in conjunction with a Philips PM8041 X-Y recorder. A two-compartment three-electrode cell was employed: the working and secondary electrodes were a platinum wire and spiral respectively. The working electrode was probed by a Luggin capillary which was connected to the reference electrode compartment. A silver-wire pseudo-reference electrode was used; potentials were calibrated using the ferrocenium–ferrocene couple.

Kinetic Measurements.—The electrochemical cell was charged with a solution of the electrolyte (20 cm^3, 0.2 mol dm^{-3} $[NBu_4][BF_4]$–thf) containing the dissolved diazenido-complex (1—5 mmol dm^{-3}). The cell and contents were equilibrated in a constant temperature bath for 30 min. Neat alkyl halide was injected into the cell *via* a septum cap using a gas-tight syringe and the reactants thoroughly mixed. The course of the alkylation reaction was monitored by cyclic voltammetry at appropriate time intervals after the initiation.

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