Chemistry and Electrochemistry of Phosphonium-functionalized Isocyanide and Derived Carbene and Indole Complexes of Group 6 Transition-metal Carbonyls

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A series of $[M(CO)_5L]$ [M = Cr, Mo or W) complexes, where L is a phosphonium-substituted phenyl isocyanide ligand of the type $o\text{-}R_3PCH_2C_6H_4NC$ [$PR_3 = PMe_3(L^1)$, $PPh_2(CH_2Ph)(L^2)$ or $PPh_3(L^3)$], have been prepared by reaction of $[NEt_4][M(CO)_5I]$ with the isocyanides in the presence of $AgBF_4$ in acetone and they have been characterized by IR, ^1H and ^{31}P NMR spectroscopies. The co-ordinated ligands L react in tetrahydrofuran at 0 °C with $Na[N(SiMe_3)_2]$ to give in most cases a mixture of different cyclization products whose structures have been assigned, on the basis of spectroscopic and electrochemical data, as the carbene-type $[M(CO)_5\{o\text{-}CNHC_6H_4C(PR_3)\}]$ **A**, indole-type $[M(CO)_5\{o\text{-}NCHC(PR_3)(C_6H_4)\}]$ **B** or protonated indole-type species $[M(CO)_5\{o\text{-}NHCHC(PR_3)(C_6H_4)\}]$ **C**. The relative abundance of the final products is strictly related to the nature of the metal and the type of R group in the phosphonium moiety: as a general trend the $[W(CO)_5L]$ complexes yield mostly type **A** derivatives, while those of Cr and Mo give primarily types **B** and **C**. A possible mechanism for the formation of these different species is discussed. These complexes, in aprotic media, exhibit upon cyclic voltammetry, a single-electron (reversible or irreversible) anodic wave, the oxidation potential of which has been applied to estimate the ligand parameters P_L and E_L for the isocyanide and derived ligands. According to their net electron-donor ability, the ligands can be ordered as follows: indoles > carbenes > protonated carbenes or protonated indoles > isocyanides. For the ligating metal centres $M(CO)_5$ (M = Mo or W) the electrochemical parameter β (polarizability) has also been estimated.

Heterocyclic carbenes can be formed by taking advantage of the reactivity of certain functionalized isocyanides which undergo intramolecular cyclization reactions when co-ordinated to electron-withdrawing metal ions. For instance, the reactions of hydroxoalkyl isocyanides of the type $HO(CH_2)_nNC$ (n = 2 or 3) with stoichiometric amounts of Pd^{II}, Pt^{II} or Au^{III} yield five-and six-membered cyclic aminooxo carbenes of the type $M{=}CNH(CH_2)_nO$ (n = 2 or 3).[1] On the other hand co-ordination to low-valent $M(CO)_5$ (M = Cr, Mo or W) metal species leads to the formation of the 'open-chain' isocyanide complexes $(OC)_5M\text{-}NC(CH_2)_nOH$.[1] As a further example, we have reported the synthesis and the co-ordination to Pt^{II} of novel functionalized isocyanides of the type $o\text{-}R_3PCH_2C_6H_4NC$ (R = alkyl or aryl);[2] treatment of the metal-co-ordinated phosphonium-substituted phenyl isocyanides with NEt_3 yields 3-(phosphonio)indolin-2-ylidene complexes of the type $[Pt{=}o\text{-}CNHC_6H_4C(PR_3)]$, which are formed as the only reaction products *via* intramolecular attack of P-ylide intermediates on the co-ordinated isocyanides.

The higher nucleophilicity of the ylidic carbanion compared to that of the hydroxyl functionality suggests that similar reactions may occur also with low-valent metal-co-ordinated phosphonium-substituted phenyl isocyanides, thus giving an entry to metal(0) heterocyclic carbenes. In this paper we report the synthesis of new phosphonium-functionalized isocyanide and derived carbene and indole complexes of Cr, Mo and W, as well as the investigation of their electrochemical behaviour which appears to have been undertaken for the first time for complexes with such types of ligands. We aimed also to correlate the redox properties of these compounds with the electron donor/acceptor ability of these ligands, in view of the known success of this type of approach for complexes with other types of isocyanide ligands.[3–8] Moreover, this study would also extend to novel carbene complexes the still rather limited electrochemical investigation reported[9–15] for compounds with multiple metal–carbon bonds.

Experimental

General Procedures.—All reactions were carried out under a nitrogen atmosphere using Schlenk techniques. Tetrahydrofuran (thf) and Et_2O were distilled from sodium–benzophenone; acetone was dried over $CaSO_4$ and degassed before use and CH_2Cl_2 was dried over CaH_2 and distilled under N_2. All the other solvents were of reagent grade and used without further purification. The IR spectra were recorded on a Perkin Elmer 983 spectrophotometer, ^1H and ^{13}C NMR spectra on a Bruker AM-400 spectrometer and ^{31}P NMR spectra (at 32 MHz) on a Varian FT 80-A spectrometer. The elemental analyses were performed by the Department of Inorganic, Organometallic and Analytical Chemistry of the University of Padova. Melting points were obtained on a hot-plate apparatus and are uncorrected.

Electrochemistry.—The electrochemical experiments were carried out either on an EG&G PAR 173 potentiostat/galvanostat and an EG&G PARC 175 Universal programmer, or on an

HI-TEK DT 2101 potentiostat/galvanostat and an HI-TEK PP RI waveform generator. Cyclic voltammetry (CV) was undertaken in a two-compartment three-electrode cell, at a platinum-wire working electrode, probed by a Luggin capillary connected to a silver-wire pseudo-reference electrode; a platinum or tungsten auxiliary electrode was employed. Controlled-potential electrolysis (CPE) was carried out in a three-electrode H-type cell with platinum-gauze working and counter electrodes in compartments separated by a glass frit; a Luggin capillary, probing the working electrode, was connected to a silver-wire pseudo-reference electrode. Prior to the addition of the complex (for the CPE experiments), each electrolyte solution was pre-electrolysed at the appropriate potential until a constant background current. The peak potentials of the complexes were measured by cyclic voltammetry in 0.2 mol dm^{-3} NBu_4BF_4–NCMe and are quoted relative to the saturated colomel electrode (SCE) by using as internal reference the $[Fe(\eta^5\text{-}C_5H_5)_2]^{0/+}$ couple ($E_{\frac{1}{2}}{}^{ox}$ = 0.42 V *vs.* SCE). All the experiments were done under dinitrogen or argon.

Starting Complexes.—The complexes $[NEt_4][M(CO)_5I]$ (M = Cr, Mo or W)[16] and the ligands $[o\text{-}R_3PCH_2C_6H_4NC]BF_4$ [PR_3 = PMe_3 (L^1), $PPh_2(CH_2Ph)$ (L^2) or PPh_3 (L^3)][2b,c] were prepared according to published procedures.

Synthesis of Isocyanide Complexes.—$[Cr(CO)_5(o\text{-}Me_3PCH_2C_6H_4NC)]BF_4$ **1**. To a solution of $[NEt_4][Cr(CO)_5I]$ (0.671 g, 1.49 mmol) in acetone (10 cm^3) at 0 °C was added dropwise a solution of $AgBF_4$ (0.302 g, 1.55 mmol) in acetone (20 cm^3) over a period of 20 min and the system was then stirred for 5 min at room temperature. The AgI formed was filtered off and the solution was then treated dropwise at 0 °C with a solution of $[o\text{-}Me_3PCH_2C_6H_4NC]BF_4$ (0.385 g, 1.38 mmol) in acetone (20 cm^3) over a period of 20 min. The course of this reaction was followed by monitoring in the IR spectrum the decrease in the $\nu(N{\equiv}C)_{free}$ stretching at 2119 cm^{-1} and the increase in $\nu(N{\equiv}C)_{co\text{-}ord}$ at 2134 cm^{-1}. After stirring the solution at room temperature for 5 min, no residual $\nu(N{\equiv}C)_{free}$ absorption of the starting material was present. The reaction mixture was taken to dryness and the residue washed with water–hexane (1:3, 30 cm^3). The resulting solid was dissolved in CH_2Cl_2 (30 cm^3), and the solution dried over anhydrous Na_2SO_4. After filtration, the solution was taken to dryness and the residue washed with hexane (20 cm^3). The final solid product was filtered off and dried under vacuum. Yield 0.653 g (93%), m.p. 112–115 °C (Found: C, 40.60; H, 3.95; N, 3.15. Calc. for $C_{16}H_{15}BCrF_4NO_5P$: C, 40.80; H, 3.20; N, 2.95%).

$[Mo(CO)_5(o\text{-}Me_3PCH_2C_6H_4NC)]BF_4$ **2**. This compound was prepared as described for **1** starting from $[NEt_4][Mo(CO)_5I]$ (0.382 g, 0.77 mmol), an acetone solution of $AgBF_4$ (0.157 g, 0.81 mmol) and $[o\text{-}Me_3PCH_2C_6H_4NC]BF_4$ (0.200 g, 0.72 mmol). The reaction time was 5.5 h at room temperature after the addition of the isocyanide was complete. Yield 0.190 g (52%), m.p. 92–95 °C (Found: C, 37.00; H, 3.10; N, 2.75. Calc. for $C_{16}H_{15}BF_4MoNO_5P$: C, 37.30; H, 2.95; N, 2.70%).

$[W(CO)_5(o\text{-}Me_3PCH_2C_6H_4NC)]BF_4$ **3**. This compound was prepared as described for **1** starting from $[NEt_4][W(CO)_5I]$ (0.450 g, 0.77 mmol), an acetone solution of $AgBF_4$ (0.157 g, 0.81 mmol) and $[o\text{-}Me_3PCH_2C_6H_4NC]BF_4$ (0.200 g, 0.72 mmol). The reaction time was 30 min at room temperature after the addition of the isocyanide was complete. Yield 0.405 g (94%), m.p. 113–115 °C (Found: C, 31.50; H, 2.95; N, 2.35. Calc. for $C_{16}H_{15}BF_4NO_5PW$: C, 31.85; H, 2.50; N, 2.30%).

$[Cr(CO)_5\{o\text{-}(PhCH_2)Ph_2PCH_2C_6H_4NC\}]BF_4$ **4**. To a solution of $[NEt_4][Cr(CO)_5I]$ (0.316 g, 0.705 mmol) in acetone (10 cm^3) at 0 °C a solution of $AgBF_4$ (0.142 g, 0.73 mmol) in acetone (20 cm^3) was added dropwise over a period of 20 min and the reaction mixture then stirred for 5 min at room temperature. The AgI formed was filtered off and the solution was then treated dropwise at 0 °C with a solution of $[o\text{-}(PhCH_2)Ph_2PCH_2C_6H_4NC]BF_4$ (0.312 g, 0.65 mmol) dissolved in acetone (20 cm^3) over a period of 20 min. After stirring the solution at room temperature for 10 min the reaction was complete. The solution was then evaporated to dryness under vacuum. The solid residue was washed with water (3 × 10 cm^3), dissolved in CH_2Cl_2 (30 cm^3), and the solution dried over anhydrous Na_2SO_4. Work-up of the reaction mixture as described for compound **1** gave the final solid product, which was filtered off and dried under vacuum. Yield 0.360 g (83%), m.p. 93–95 °C (Found: C, 56.75; H, 3.95; N, 2.10. Calc. for $C_{32}H_{23}BCrF_4NO_5P$: C, 57.25; H, 3.45; N, 2.10%).

$[Mo(CO)_5\{o\text{-}(PhCH_2)Ph_2PCH_2C_6H_4NC\}]BF_4$ **5**. To a solution of $[NEt_4][Mo(CO)_5I]$ (0.493 g, 1.00 mmol) in acetone (10 cm^3) at −8 °C a solution of $AgBF_4$ (0.202 g, 1.04 mmol) in acetone (20 cm^3) was added dropwise over a period of 20 min and the reaction mixture was then stirred for 5 min at room temperature. The AgI formed was filtered off and the solution was then treated dropwise at 0 °C with a solution of $[o\text{-}(PhCH_2)Ph_2PCH_2C_6H_4NC]BF_4$ (0.443 g, 0.925 mmol) dissolved in acetone (20 cm^3) over a period of 20 min. After stirring the solution at room temperature for 1 h the reaction was complete. The reaction mixture was worked up as described for compound **4**, and the final solid product was filtered off and dried under vacuum. Yield 0.543 g (83%), m.p. 110–112 °C (Found: C, 54.05; H, 3.75; N, 2.00. Calc. for $C_{32}H_{23}BF_4MoNO_5P$: C, 53.75; H, 3.25; N, 1.95%).

$[W(CO)_5\{o\text{-}(PhCH_2)Ph_2PCH_2C_6H_4NC\}]BF_4$ **6**. This compound was prepared as described for **4** starting from $[NEt_4][W(CO)_5I]$ (0.581 g, 1.00 mmol), an acetone solution of $AgBF_4$ (0.202 g, 1.04 mmol) and $[o\text{-}(PhCH_2)Ph_2PCH_2C_6H_4NC]BF_4$ (0.443 g, 0.92 mmol). The reaction time was 10 h at room temperature after the addition of the isocyanide was complete. Yield 0.680 g (92%), m.p. 102–105 °C (Found: C, 47.60; H, 3.40; N, 1.70. Calc. for $C_{32}H_{23}BF_4NO_5PW$: C, 47.85; H, 2.90; N, 1.75%).

$[Cr(CO)_5\{o\text{-}Ph_3PCH_2C_6H_4NC\}]BF_4$ **7**. This compound was prepared as described for **4** starting from $[NEt_4][Cr(CO)_5I]$ (0.224 g, 0.50 mmol), an acetone solution of $AgBF_4$ (0.101 g, 0.52 mmol) and $[o\text{-}Ph_3PCH_2C_6H_4NC]BF_4$ (0.215 g, 0.46 mmol). The reaction time was 30 min after the addition of the isocyanide was complete. Yield 0.245 g (80%), m.p. 103–106 °C (Found: C, 56.05; H, 3.85; N, 2.15. Calc. for $C_{31}H_{21}BCrF_4NO_5P$: C, 56.65; H, 3.20; N, 2.15%).

$[Mo(CO)_5(o\text{-}Ph_3PCH_2C_6H_4NC)]BF_4$ **8**. This compound was prepared as described for **4** starting from $[NEt_4][Mo(CO)_5I]$ (0.493 g, 1.00 mmol), an acetone solution of $AgBF_4$ (0.202 g, 1.04 mmol) and $[o\text{-}Ph_3PCH_2C_6H_4NC]BF_4$ (0.430 g, 0.925 mmol). The reaction time was 5 min at room temperature after the addition of the isocyanide was complete. Yield 0.476 g (74%), m.p. 122–126 °C (Found: C, 53.75; H, 3.85; N, 2.10. Calc. for $C_{31}H_{21}BF_4MoNO_5P$: C, 53.10; H, 3.00; N, 2.00%).

$[W(CO)_5(o\text{-}Ph_3PCH_2C_6H_4NC)]BF_4$ **9**. This compound was prepared as described for **4** starting from $[NEt_4][W(CO)_5I]$ (0.581 g, 1.00 mmol), an acetone solution of $AgBF_4$ (0.202 g, 1.04 mmol) and $[o\text{-}Ph_3PCH_2C_6H_4NC]BF_4$ (0.430 g, 0.925 mmol). The reaction time was 2 h at room temperature after the addition of the isocyanide was complete. Yield 0.604 g (83%), m.p. 112–115 °C (Found: C, 47.05; H, 3.00; N, 1.90. Calc. for $C_{31}H_{21}BF_4NO_5PW$: C, 47.20; H, 2.70; N, 1.75%).

Reactions of Isocyanide Complexes with $Na[N(SiMe_3)_2]$.—$[Cr(CO)_5\{o\text{-}\overline{CNHC_6H_4C}(PMe_3)\}]$ **10**. To a yellow solution of compound **1** (0.400 g, 0.85 mmol) in thf (40 cm^3) was added dropwise at 0 °C a solution of $Na[N(SiMe_3)_2]$ (0.768 g, 0.85 mmol) in thf (10 cm^3). After 1 h the ice-bath was removed and the stirring was continued at room temperature for 1 h. An examination of the IR spectrum of the solution did not reveal any N≡C band due to the starting complex. The solution was then evaporated to dryness under vacuum. The solid residue was washed with water (3 × 10 cm^3), dissolved in CH_2Cl_2 (50 cm^3), and the solution dried over anhydrous Na_2SO_4. After filtration, the solvent was evaporated under reduced pressure and the residue washed with pentane (30 cm^3). The final solid product was filtered off and dried under vacuum. Yield 0.229 g (71%), m.p. 212–215 °C (decomp.) (Found: C, 49.90; H, 4.00; N, 3.70. Calc. for $C_{16}H_{14}CrNO_5P$: C, 50.15; H, 3.70; N, 3.65%).

Compound **11**. This reaction was carried out as described for **10** starting from complex **2** (0.141 g, 0.27 mmol) and a solution of $Na[N(SiMe_3)_2]$ (0.244 g, 0.27 mmol) in thf (20 cm^3). The reaction time was 15 min at 0 °C and 5 min at room temperature. Spectroscopic data indicate that **11** is a mixture of structurally different products (see text). Yield 0.090 g.

$[W(CO)_5\{o\text{-}\overline{CNHC_6H_4C}(PMe_3)\}]$ **12**. This compound was prepared as described for **10** starting from complex **3** (0.300 g, 0.50 mmol) and a solution of $Na[N(SiMe_3)_2]$ (0.442 g, 0.50 mmol) in thf (30 cm^3). The reaction time was 15 min at 0 °C and 45 min at room temperature. Yield 0.188 g (74%), m.p. 137–140 °C (Found: C, 36.90; H, 3.20; N, 2.75. Calc. for $C_{16}H_{14}NO_5PW$: C, 37.30; H, 2.75; N, 2.70%).

Compound **13**. This reaction was carried out as described for **10** starting from complex **4** (0.294 g, 0.44 mmol) and a solution of $Na[N(SiMe_3)_2]$ (0.397 g, 0.44 mmol) in thf (30 cm^3). The reaction time was 30 min at 0 °C and 30 min at room temperature. Spectroscopic data indicate that **13** is a mixture of structurally different products (see text). Yield 0.194 g.

Compound **14**. To a thf suspension (20 cm^3) of compound **5** (0.293 g, 0.41 mmol) cooled at −40 °C was added dropwise a solution of $Na[N(SiMe_3)_2]$ (0.371 g, 0.41 mmol) in thf (10 cm^3). The stirred solution was allowed to warm slowly to room temperature. After 2 h at room temperature an IR spectrum showed that (almost) all the starting complex had reacted. Then the reaction mixture was worked up as described for **10** and the final solid products were filtered off and dried under vacuum. Spectroscopic data indicate that **14** is a mixture of structurally different products (see text). Yield 0.184 g.

$[W(CO)_5\{o\text{-}\overline{CNHC_6H_4C}[PPh_2(CH_2Ph)]\}]$ **15**. This compound was prepared as described for **10** starting from complex **6** (0.464 g, 0.58 mmol) and a solution of $Na[N(SiMe_3)_2]$ (0.524 g, 0.58 mmol) in thf (30 cm^3). The reaction time was 1 h at 0 °C and 45 min at room temperature. Yield 0.309 g (75%), m.p. 122–125 °C (Found: C, 53.80; H, 3.65; N, 2.00. Calc. for $C_{32}H_{22}NO_5PW$: C, 53.70; H, 3.10; N, 1.95%).

Compound **16**. This compound was prepared as described for **10** starting from complex **7** (0.165 g, 0.25 mmol) and a solution of $Na[N(SiMe_3)_2]$ (0.226 g, 0.25 mmol) in thf (15 cm^3). The reaction time was 10 min at 0 °C and 3 h at room temperature. Spectroscopic data indicate that **16** is a mixture of structurally different products (see text). Yield 0.115 g.

Compound **17**. This reaction was carried out as described for **14** starting from complex **8** (0.367 g, 0.52 mmol) and a solution of $Na[N(SiMe_3)_2]$ (0.470 g, 0.52 mmol) in thf (30 cm^3). The reaction time was 30 min at −40 °C and 1.5 h at room temperature. Spectroscopic data indicate that **17** is a mixture of structurally different products (see text). Yield 0.190 g.

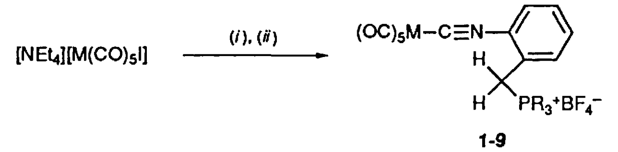
$[W(CO)_5\{o\text{-}\overline{CNHC_6H_4C}(PPh_3)\}]$ **18**. This compound was prepared as described for **10** starting from complex **9** (0.402 g, 0.51 mmol) and a solution of $Na[N(SiMe_3)_2]$ (0.461 g, 0.51 mmol) in thf (30 cm^3). During the base addition the colour of the solution changes from light to dark yellow. The reaction time was 1.5 h at 0 °C and 2.5 h at room temperature. Yield 0.25 g (70%), m.p. 130–133 °C (Found: C, 53.50; H, 3.00; N, 2.00. Calc. for $C_{31}H_{20}NO_5PW$: C, 53.10; H, 2.85; N, 2.00%).

Chemical Studies

Results.—Preparation of $[M(CO)_5L]$ *complexes.* The carbonyl isocyanide complexes **1**–**9** are prepared in acetone at room temperature by metathesis reactions starting from $[NEt_4][M(CO)_5I]$, $AgBF_4$ and the appropriate ligand L^1–L^3 as outlined in Scheme 1. Derivatives **1**–**9** are obtained in good yield (52–94%) as yellow crystalline solids stable in the solid state and in solution. Their structure was established on the basis of elemental analysis (see Experimental section), IR and NMR data (Table 1).

In the IR spectra, either as a Nujol mull or acetone solution, the $\nu(C{\equiv}N)$ stretching appears as a medium-intensity band at a slightly higher wavelength (12–18 cm^{-1}) with respect to that of the free isocyanide ligands L^1–L^3. The ^1H NMR spectra display the CH_2 resonance as a doublet by coupling with the adjacent phosphorus atom in the range δ 3.86 (complex **1**)–5.11 (complex **8**). In the $^{31}P\text{-}\{^1H\}$ NMR spectra the compounds **1**–**3** and **7**–**9** show the expected single resonance for the phosphonium group in the range δ 22.68–29.27 relative to H_3PO_4, while **4**–**6** exhibit two close, distinct and sharp signals probably arising from two different phosphonium conformational isomers.

Cyclization reaction. (*a*) *General.* The cyclization reactions of complexes **1**–**9** (Scheme 2) were carried out in thf using stoichiometric amounts of $Na[N(SiMe_3)_2]$ as the base. The progress of the reaction was monitored by following the disappearance of the $\nu(C{\equiv}N)$ stretching in the IR spectrum. The reactions were stopped about 5 min after the complete disappearance of this band since a prolonged reaction time gives rise to further bands in the $\nu(CO)$ region due to not well defined compounds. The crude products obtained after evaporation of the solvent from the reaction mixture were washed with water to dissolve the

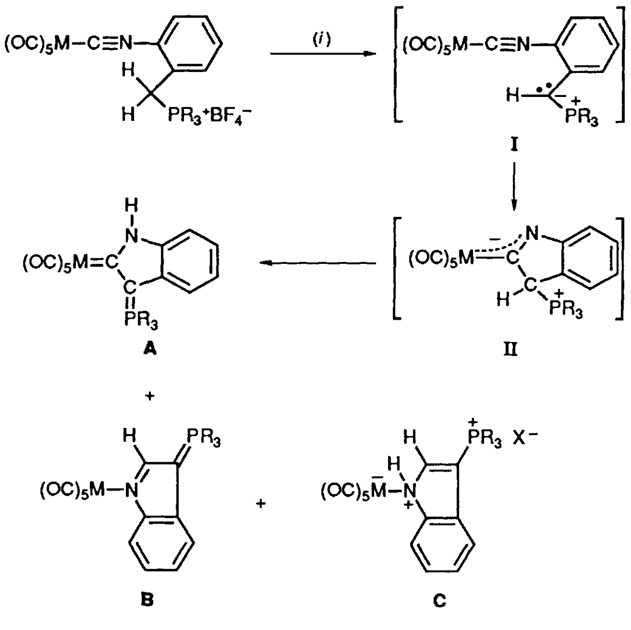


1-9

	PR$_3$		
M	PMe$_3$	PPh$_2$(CH$_2$Ph)	PPh$_3$
Cr	**1** (**10**)	**4** (**13**)	**7** (**16**)
Mo	**2** (**11**)	**5** (**14**)	**8** (**17**)
W	**3** (**12**)	**6** (**15**)	**9** (**18**)

Compounds **10**–**18** are the reaction products of **1**–**9** with $Na[N(SiMe_3)_2]$

Scheme 1 (*i*) $AgBF_4$, −AgI, $-NEt_4BF_4$, acetone, 0 °C; (*ii*) L, 0–25 °C, acetone



Scheme 2 (*i*) $Na[N(SiMe_3)_2]$, $-NH(SiMe_3)_2$, $-NaBF_4$, room temperature

Table 1 Infrared, ^1H and ^{31}P-{^1H} NMR spectroscopic data for compounds $[M(CO)_5(o\text{-}R_2R'PCH_2C_6H_4NC)]BF_4$

				IR [a]/cm^{-1}	^1H NMR [b]				
Compound	M	R	R′	ν(C≡N)	δ(CH_2)	^2J(HP)	δ(R)	^2J(HP)	δ(^{31}P) [c]
1 [d]	Cr	Me	Me	2137s	3.86 (d)	15.7	1.94 (d)	14.0	29.27 (s)
				2134s					
2 [d]	Mo	Me	Me	2138s	3.87 (d)	15.7	1.95 (d)	13.9	29.27 (s)
				2135s					
3 [d]	W	Me	Me	2139s	3.87 (d)	15.8	1.95 (d)	13.9	29.16 (s)
				2136s					
4	Cr	Ph	CH_2Ph	2135s	4.70 (d)	14.0			26.18 (s)
				2132s	4.62 (d)	14.3			25.20 (s)
5	Mo	Ph	CH_2Ph	2134s	4.84 (d)	14.7			26.14 (s)
				2133s	4.70 (d)	13.8			25.19 (s)
6	W	Ph	CH_2Ph	2135s	4.77 (d)	14.5			25.93 (s)
				2134s	4.64 (d)	13.7			24.89 (s)
7	Cr	Ph	Ph	2133s	5.06 (d)	14.4			22.68 (s)
				2132s					
8	Mo	Ph	Ph	2134s	5.11 (d)	14.4			22.69 (s)
				2133s					
9	W	Ph	Ph	2135s	5.01 (d)	14.2			22.69 (s)
				2134s					

[a] First value for Nujol mull, second for acetone solution; s = strong. [b] In $CDCl_3$ unless otherwise stated; d = doublet; J in Hz. Recorded in $CDCl_3$ using $SiMe_4$ as internal standard. [c] In $CDCl_3$ unless otherwise stated; s = singlet. Phosphorus chemical shifts referenced to external H_3PO_4 (85%). [d] Spectra recorded in CD_2Cl_2; proton chemical shifts are reported relative to $SiMe_4$ by taking the chemical shift of CD_2Cl_2 as + 5.32 ppm.

Table 2 Infrared, ^1H and ^{31}P-{^1H} NMR spectroscopic data for compounds in Scheme 2

	IR [a]/cm^{-1}	^1H NMR [b]			
Compound	ν(N–H)	δ(NH)	δ(R)	^2J(HP)	δ(^{31}P) [c]
10 [d]	3460s	8.97 (br)	2.23 (d)	13.4	9.98 (s)
11 [d]			2.05 (d)	13.6	3.43 (s)
12 [d]	3459s	8.93 (br)	2.23 (d)	13.5	10.40 (s)
13			4.25 (d)	14.1	9.72 (s)
14			4.26 (d)	14.0	9.92 (s)
			4.43 (d)	13.3	12.91 (s)
15			4.26 (d)	14.2	9.91 (s) [e]
			4.37 (d)	13.9	12.90 (s) [e]
	3452s	9.28 (br)	4.86 (d)	15.4	14.68 (s)
16					10.71 (s)
					13.33 (s, br)
17					10.89 (s)
					13.21 (s)
18					13.09 (s) [e]
	3433s	9.21 (br)			14.19 (s)

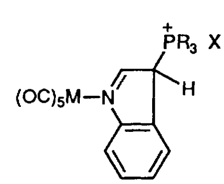
[a] Nujol mull; s = strong. [b] In $CDCl_3$ unless otherwise stated; br = broad; J in Hz. Recorded in $CDCl_3$ using $SiMe_4$ as internal standard. [c] In $CDCl_3$ unless otherwise stated; phosphorus chemical shifts referenced to external H_3PO_4 (85%). [d] Spectra recorded in CD_2Cl_2; proton chemical shifts are reported relative to $SiMe_4$ by taking the chemical shift of CD_2Cl_2 as + 5.32 ppm. [e] Small amounts.

inorganic salts and recrystallized from CH_2Cl_2–hexane. The analysis of the spectroscopic and electrochemical data suggests that the final products are often a mixture of species having a structure of type **A**–**C** the relative abundance of which is strictly related to the nature of the metal and the type of R groups in the phosphonium moiety as described in detail below.

(*b*) $[W(CO)_5L]$ *systems*. The cyclization reactions of the tungsten complexes **3**, **6** and **9** lead to the formation of complexes **12**, **15** and **18** as main products for which the carbene-type structure **A** has been assigned on the basis of IR and NMR (^1H, ^{31}P-{^1H} and, in some cases, ^{13}C-{^1H}) spectroscopic data. The IR spectra (Nujol mull) show a strong band in the range 3459–3433 cm^{-1} attributable to a NH group; this latter shows up as a broad resonance between δ 8.93 and 9.21 in the ^1H NMR spectra. The ^{31}P NMR spectra display a singlet at δ 10.40 (**12**), 14.68 (**15**) and 14.19 (**18**). These spectroscopic data match closely those of the corresponding cyclic platinum(II) derivatives which were obtained using NEt_3 as the base.[2] In addition, the ^{13}C-{^1H} NMR spectra of complexes **12** and **15** confirm the presence of a metal-co-ordinated carbene carbon atom at δ 183.07 [^1J(CW) = 96.58, ^2J(CP) = 39.44 Hz] and 178.17 [^1J(CW) not observed, ^2J(CP) = 42.86 Hz], respectively. These chemical shifts are in very good agreement with tungsten complexes having a co-ordinated heterocyclic carbene system.[17] The cyclic compounds **12** and **18** are protonated by addition of HBF_4 (ether solution) giving rise in their ^{31}P-{^1H} NMR spectra to a signal at δ 27.88 and 22.68, respectively. The downfield shift of the phosphorus atom suggests that the protonation occurs at the β position of the indole ring with formation of a $^+PR_3$ group as observed also with platinum(II) derivatives;[2] however, the protonated tungsten compounds are not stable and rapidly decompose to unidentified species.

(*c*) $[Cr(CO)_5L]$ *and* $[Mo(CO)_5L]$ *systems*. These reactions give different and, in some cases, more complicated final mixtures of complexes than those obtained from the analogous tungsten compounds. Thus, the reaction product of **7** with $Na[N(SiMe_3)_2]$ shows two resonances in the ^{31}P-{^1H} NMR spectrum at δ 10.71 and 13.33 (the latter species being the major product), while complex **4** forms derivative **13** which shows in the ^{31}P-{^1H} NMR spectrum only one resonance at δ 9.72. It is noteworthy that the same mixture obtained from **7** and $Na[N(SiMe_3)_2]$ was also formed by direct reaction of the '$[Cr(CO)_5(solv)]$' species with the free cyclic indole $\overline{N(o\text{-}C_6H_4)C(PPh_3)C}H$, independently prepared by cyclization of the corresponding free isocyanide ligand with $Na[N(SiMe_3)_2]$ in thf solution. By analogy with similar reactions of platinum(II) substrates with the same indole ligand leading to *N*-co-ordinated indole derivatives,[2b] it is reasonable to assume also in these chromium products the formation of a M–N(indole) bond (type **B** structure, Scheme 2). This suggestion is strengthened by the absence of the ν(N–H) stretching and the NH resonance in the IR and ^1H NMR spectra, respectively, of the cyclization products of complexes **4** and **7**. Conversely, compound **1** reacts with $Na[N(SiMe_3)_2]$ to generate a product showing in the ^{31}P-{^1H} NMR spectrum a single resonance at δ 9.98 (*i.e.* at a chemical shift similar to that found for the tungsten derivative, see Table 2). Furthermore, in the ^{1}H NMR spectrum a broad resonance is observed at δ 8.97 and in the IR spectrum a strong band appears at 3460 cm^{-1} suggesting the presence of a NH group. Further spectroscopic support for the carbene-like **A** structure for this derivative is given by the ^{13}C-{^{1}H} NMR spectrum which exhibits a carbene-carbon chemical shift at δ 191.77 [^2J(CP) = 42.24 Hz] and an ylide carbon resonance at δ 97.66 [^1J(CP) = 125.75 Hz]. Again, this compound reacts with HBF_4 to give rise in the ^{31}P-{^{1}H} NMR spectrum to a signal at δ 28.66 which is characteristic for β protonation of a structure of type **A**.

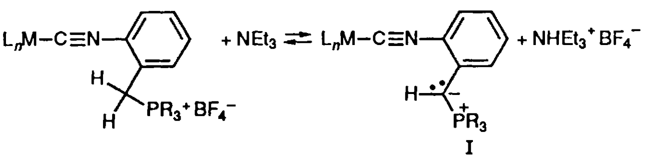
The cyclization reaction of the pentacarbonylmolybdenum-co-ordinated isocyanide ligands **5** and **8** gives in both cases a mixture of two compounds which are tentatively formulated as having type **B** and **C** structures. The ^{31}P-{^{1}H} NMR spectra show two signals at δ 9.92, 12.91 and 10.89, 13.21, respectively, while the derivative **11** is the only product formed by cyclization of compound **2**. By treatment of the mixtures with a few drops of an ether solution of HBF_4 the signal at higher field in the ^{31}P-{^{1}H} NMR spectrum disappears while the signal at lower field increases. The former is regenerated upon addition of KOH in acetone solution thus suggesting an acid–base equilibrium between the two species. Analogous behaviour is also observed for the chromium compounds **13** and **16**. The protonated structure **C** (Scheme 2) is preferred with respect to the possible structure **D**, protonated on the ylidic carbon, on the basis of ^{31}P-{^{1}H} and ^{13}C-{^{1}H} NMR evidence.



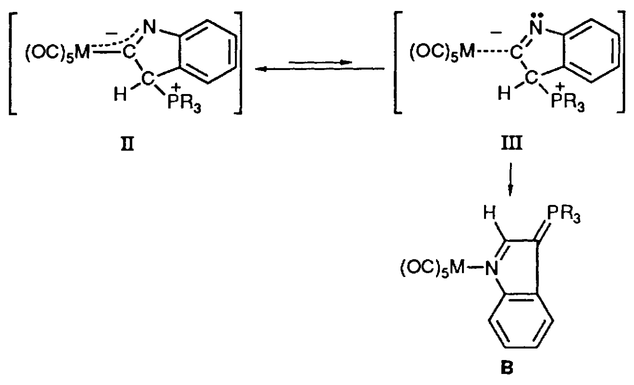
D

For complex **17** the resonances observed in the ^{31}P-{^{1}H} and in the ^{13}C-{^{1}H} NMR spectra, at δ 13.21 and 85.56 [^1J(CP) = 120.07 Hz] for the ylidic carbon atom, respectively, are very close to those of the corresponding protonated free ligand which shows resonances at δ 13.16 and 84.60 [^1J(CP) = 119.57 Hz] respectively for X = BF_4. On the contrary, in the case of structure **D** a lower-field value for the ^{31}P-{^{1}H} NMR[2b] and a higher-field chemical shift for the sp^3 ylidic carbon atom are expected.

Discussion.—Although structurally different compounds are formed by the cyclization processes in Scheme 2, a common reaction for all the starting metal-co-ordinated isocyanide complexes, when treated with a base, is the initial formation of a ylide functionality (intermediate **I**) derived by deprotonation of the phosphonium group, and the subsequent intramolecular nucleophilic attack on the co-ordinated isocyanide carbon atom (intermediate **II**). It is worth noting that the co-ordination of isocyanides to the 'M(CO)$_5$' organometallic fragments does not activate these ligands towards nucleophilic attack to the same extent as in platinum(II) complexes. The values of $\Delta\nu(C{\equiv}N) = \nu(C{\equiv}N)_{\text{co-ord}} - \nu(C{\equiv}N)_{\text{free}}$,[18] which can be taken as indicators of the electrophilicity of the metal-co-ordinated isocyanide carbon,[19] range between 80 and 90 cm^{-1} for [PtL$_n$-(C≡NC$_6$H$_4$CH$_2$PR$_3$$^+$-*o* X$^-$)] complexes[2] but drop to only 12–18 cm^{-1} in the present [M(CO)$_5$(C≡NC$_6$H$_4$CH$_2$PR$_3$$^+$-*o* X$^-$)] (M = Cr, Mo or W) systems, thus indicating a very low electrophilic character of the isocyanide carbon in these compounds. This intrinsic different activation of the co-ordinated isocyanide ligands in complexes of Pt^{II} and M^0 requires an appropriate choice of the base to promote the subsequent cyclization reaction. While platinum(II) complexes immediately react with NEt_3 to form the final heterocyclic systems, for the carbonyl metal-co-ordinated isocyanides a stronger base such as Na[N(SiMe$_3$)$_2$] is necessary for a complete cyclization reaction. Thus, when the phosphonium system is treated with NEt_3 the acid–base equilibrium in Scheme 3 is established. The formation of the ylidic intermediate **I** in highly activated platinum(II) complexes is rapidly followed by nucleophilic attack of the ylide on the co-ordinated isocyanide carbon atom, thus shifting the reaction to the right. On the contrary, in the pentacarbonylmetal complexes the presence of an adjacent low activated co-ordinated isocyanide ligand makes the ylide sufficiently long-lived to be reprotonated by the triethylammonium acid, restoring the starting phosphonium complex. Conversely, when Na[N(SiMe$_3$)$_2$] is used as the base, the conjugate acid NH(SiMe$_3$)$_2$ is not sufficiently strong to protonate the ylide, which only can react with the co-ordinated isocyanide group to give the indolic intermediate **II** (Scheme 2). This latter then turns into different products depending on the nature of the metal centre and the type of R groups on the phosphonium moiety.



Scheme 3



Scheme 4

The proton shift from the phosphonium group to the imino nitrogen of intermediate **II** may account for the formation of type **A** complexes (Scheme 2); a similar mechanism was proposed also for the platinum(II) systems, but in the latter case the hydrogen transfer is facilitated by the presence of NEt_3 which acts as a catalyst for the 1,3-hydrogen shift through the $NEt_3/NHEt_3^+$ couple.[2] The success of this transformation can be related to the stability of the M–C bond in the intermediate **II**, which for Group 6 metal complexes varies as follows: W > Cr > Mo.[20] Thus, the high W–C bond strength in the cyclic intermediate could favour the 1,3-proton shift from the ylide carbon to the nitrogen atom with the formation of the type **A** carbene, the primary product obtained with tungsten isocyanides. However, spectroscopic data indicate the formation of very small amounts (< 2%) of two other products, analogous to those obtained by cyclization of complexes of Cr and Mo, suggesting that also for W alternative routes are operative during the cyclization process. In the case of isocyanide complexes of Cr and Mo the IR and NMR data clearly suggest that the heterocycle system formed does not have a type **A** but rather a type **B** structure (Scheme 2).

A possible pathway leading to the formation of the metal N-co-ordinated indolyl ligand **B** may involve a concerted mechanism with M–C bond weaking and 1,2-hydrogen shift from the ylidic to the carbene carbon (Scheme 4). The formation of heteroatom-co-ordinated metal complexes by M–C bond breaking in unstable intermediates was previously reported. For instance, Bartel and Fehlhammer,[1a] in order to justify the isolation of 2-oxazoline in the catalytic reaction between

Table 3 Summary of electrochemical data for phosphonium-functionalized isocyanide complexes $[M(CO)_5(o\text{-}R_3PCH_2C_6H_4NC)]BF_4$ and derived carbene $[M(CO)_5\{o\text{-}CNHC_6H_4C(PR_3)\}]$, indole $[M(CO)_5\{o\text{-}N{=}CHC(PR_3)(C_6H_4\}]$, protonated carbene and protonated indole $[M(CO)_5\{o\text{-}NHCH{=}C(PR_3)(C_6H_4\}]^+$ complexes

Complex Type	M	PR_3	$E_{p/2}^{ox}$ $(E_{\frac{1}{2}}^{ox})^a$/V
Isocyanide	Cr	PMe_3	(1.14)
	Cr	$PPh_2(CH_2Ph)$	(1.20)
	Mo	$PPh_2(CH_2Ph)$	1.13
	Mo	PPh_3	1.22
	W	$PPh_2(CH_2Ph)$	1.24
	W	PPh_3	1.25
Carbene	Cr	PMe_3	(0.63)
	Cr	$PPh_2(CH_2Ph)$	(0.68)[b]
	W	PMe_3	0.77
	W	$PPh_2(CH_2Ph)$	0.70
	W	PPh_3	(0.79)
Indole	Cr	$PPh_2(CH_2Ph)$	(0.58)
	Mo	PMe_3	(0.65)
	Mo	$PPh_2(CH_2Ph)$	0.55[c]
	Mo	PPh_3	0.55
Protonated carbene[d]	Cr	PMe_3	(0.90)
	W	PMe_3	1.07
	W	$PPh_2(CH_2Ph)$	1.06
	W	PPh_3	1.06
Protonated indole[d]	Cr	$PPh_2(CH_2Ph)$	(0.88)
	Mo	PMe_3	1.06
	Mo	PPh_3	0.93

[a] Values in V ± 0.2, *vs.* SCE measured at a platinum electrode by CV at 100 mV s^{-1}, in 0.2 mol dm^{-3} $NBu^n{}_4BF_4$–NCMe (complex concentration *ca.* 1.5 mmol dm^{-3}), by using as internal reference the couple $[Fe(\eta^5\text{-}C_5H_5)_2]^{0/+}$ with $E_{\frac{1}{2}}^{ox}$ = 0.42 V *vs* SCE. For the reversible processes, the $E_{\frac{1}{2}}^{ox}$ values are indicated in parentheses. [b] Complex generated *in situ* upon addition of 0.1 mol dm^{-3} $NBu^n{}_4OH$ in MeOH (1 equivalent) to the solution of the corresponding isocyanide complex. [c] Complex generated *in situ* upon addition of 1.4 mol dm^{-3} $LiBu^n$ in hexane (1 equivalent) to the solution of the corresponding isocyanide complex. [d] Complexes generated *in situ* upon addition of $[Et_2OH]BF_4$ (1 equivalent) to the corresponding indole or carbene parent complexes.

$ZnSO_4$ or $PdCl_2$ and 2-hydroxyethyl isocyanide, proposed a mechanism involving initially a *C*-co-ordinated intermediate, which then rapidly isomerizes to a N-co-ordinated species *via* 1,2-hydrogen shift and M–C bond breaking. This species was isolated in the stoichiometric reaction between $ZnSO_4$ and the isocyanide. Similar rearrangements were also reported to take place in the reactions of (alkylthiocarbene)- or (aminocarbene)-pentacarbonyl metal (M = Cr or W) complexes with HX (X = Cl or Br),[21] in the reactions of $[Cr(CO)_5\{CMe(OMe)\}]$ with substituted hydrazines or hydroxylamine[22] and, finally, in the reaction of $[Cr(CO)_5\{CPh(OMe)\}]$ with PMe_2H.[23]

Electrochemical Studies

General.—The redox properties of most of the above-mentioned complexes have been studied by cyclic voltammetry, in 0.2 mol dm^{-3} NBu_4BF_4–NCMe, at a platinum electrode. They undergo a single-electron (also confirmed by controlled-potential electrolysis), reversible or irreversible, anodic process which, as for many other 18-electron complexes with $M(CO)_5$ (M = Cr, Mo or W) metal sites,[3,6,9,24,25] should correspond to the expected $M^0 \longrightarrow M^I$ oxidation; this is commonly followed, at a higher potential, by a second (irreversible) anodic process which has not been investigated further.

The values of the oxidation potential for the first wave ($E_{\frac{1}{2}}^{ox}$ or $E_{p/2}^{ox}$/V *vs.* SCE, the latter for the irreversible processes, see Table 3) lie in the ranges 1.3–1.1 (isocyanide complexes) > 1.1–0.9 (protonated indole and protonated carbene complexes) > 0.8–0.6 (carbene complexes) > 0.6–0.5 V (indole complexes), therefore suggesting the following order for the net electron-donor ability of the corresponding ligands: indoles > carbenes > protonated indoles, protonated carbenes > isocyanides. Moreover, within the same type of ligands (*e.g.* isocyanides), the tungsten complexes present higher anodic potentials than their molybdenum or chromium analogues. This relative behaviour, for W and Mo, follows the $M^0 \longrightarrow M^I$ ionization potential in the gas phase[26] and parallels that observed[4] for the series *trans*-$[M(CNR)_2(Ph_2PCH_2CH_2PPh_2)_2]$ (M = Mo or W); however, it disagrees with that for other carbonyl isocyanide complexes such as $[M(CNBu^t)_n(CO)_{6-n}]$ (n = 2 or 3) in which the oxidation potential decreases in the order Mo > W > Cr.[3]

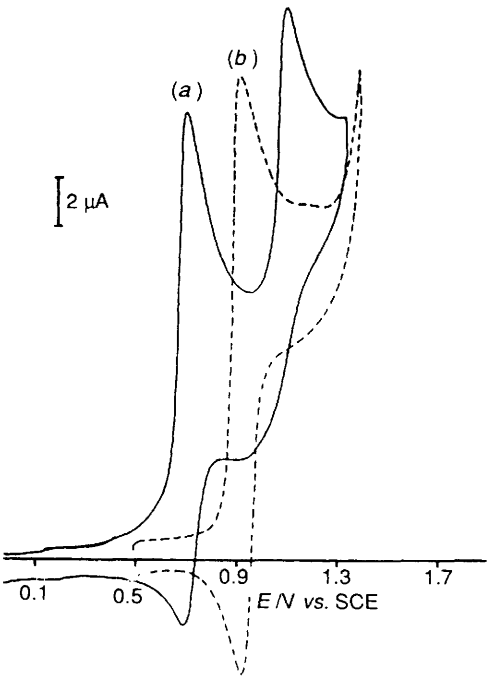
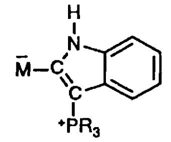


Fig. 1 Cyclic voltammograms for the carbene complex $[Cr(CO)_5\{CNHC_6H_4C(PMe_3)\}]$ (*a*) and the derived protonated species (*b*) formed upon addition of HBF_4 (1 equivalent), at a platinum electrode, in 0.2 mol dm^{-3} $NBu^n{}_4BF_4$–NCMe

For the functionalized isocyanide compounds $[M(CO)_5(o\text{-}R_3PCH_2C_6H_4NC)]BF_4$ the oxidation potentials are only slightly higher than those commonly found in related non-functionalized aromatic isocyanide complexes, *e.g.* $[Cr(CO)_5(CNC_6H_4Me\text{-}4)]$ ($E_{\frac{1}{2}}^{ox}$ = 1.14 V),[3] thus suggesting that the phosphonium group does not have a relevant effect on the metal-centred anodic process, possibly as a result of its considerable distance from the metal. Nevertheless, changes in the phosphonium moiety (PR_3^+) lead to small variations of the oxidation potential which, for the isocyanide complexes, appear to follow the expected electronic effect of the organic groups, *i.e.* the potential increases in the order $PMe_3^+ < PPh_2(CH_2Ph)^+ < PPh_3^+$. As described above, deprotonation of the isocyanide complexes leads to the formation of neutral cycloaminocarbene or indole compounds of the types $[M(CO)_5\{o\text{-}CNHC_6H_4C(PR_3)\}]$ or $[M(CO)_5\{o\text{-}N{=}CHC(PR_3)(C_6H_4)\}]$, respectively, which present oxidation potentials [Table 3 and Fig. 1(*a*)] shifted to much less anodic values (by *ca.* 0.5 or 0.6–0.7 V, respectively). Therefore, both carbenes and indoles (and mainly the latter ligands) present a much higher net electron-releasing ability than their parent ligating isocyanides.

Compared to other aminocarbenes of the type $[Cr(CO)_5\{C(NRR')Y\}]$ (R,R′ or Y = H, alkyl, aryl or related group),[9] the present chromium carbene complexes exhibit oxidation potentials ($E_{\frac{1}{2}}^{ox}$ 0.68–0.63 V) somewhat lower than those of the former species ($E_{\frac{1}{2}}^{ox}$ 0.75–0.70 V), suggesting a considerable contribution from the phosphonium form with localization of negative charge at the metal. The electrochemical studies of the



carbene and indole complexes reported herein have been performed in various cases on both the previously isolated genuine samples and the species which have been generated *in situ* upon addition of a base, such as $LiBu^n$–hexane or $NBu^n{}_4OH$–MeOH, to the electrolytic NCMe solution of the parent isocyanide complexes; the values of the oxidation potentials measured in these ways agree within the experimental error.

In the latter case, the anodic wave of the initial isocyanide complex disappeared upon addition of the base, with the concomitant appearance, at a different potential, of that of the corresponding derived carbene or indole species. Moreover, following this type of procedure, by addition of an alcoholic solution of $NBu^n{}_4OH$ (1 equivalent) to the electrolytic solution of $[Cr(CO)_5\{o\text{-}Ph_2(PhCH_2)PCH_2C_6H_4NC\}]BF_4$, we have observed the generation *in situ* of the corresponding carbene complex, as detected by its anodic wave at the expected value (0.68 V) of $E_{\frac{1}{2}}^{ox}$, rather than the formation of the indole compound ($E_{\frac{1}{2}}^{ox}$ = 0.58 V) which was the product isolated from the deprotonation reaction of the isocyanide complex by $Na[N(SiMe_3)_2]$ in thf. The carbene was also not the product obtained from the addition of $LiBu^n$ in hexane to the electrolytic solution of the isocyanide complex, and these observations suggest that the presence of the alcohol conceivably favours the route to the carbene product.

Both the carbene and the indole complexes can undergo protonation reactions, the former possibly occurring at the β-carbon of the carbene ring (although the products have not been isolated) and the latter at the indole-nitrogen atom (to give products with the type **C** structure), as discussed above.

The protonated products were generated *in situ* {by addition of $[Et_2OH]BF_4$ (1 equivalent) to the electrolytic solutions of the corresponding parent complexes in NCMe} and detected by the appearance of the corresponding CV anodic waves which replaced those of the parent species (Fig. 1). The latter were regenerated (as indicated by the reappearance of their CV anodic waves) upon subsequent addition of a base (such as $NBu^n{}_4OH$, in an excess relative to the previously added acid) to the solution of the protonated species, in the case of the protonated indole–indole system; therefore, a reversible protonation–deprotonation process [equation (1)] has been recognized. However,

$$[M(CO)_5\{o\text{-}\overline{N{=}CHC(PR_3)(C}_6H_4)\}] \underset{-H^+}{\overset{H^+}{\rightleftarrows}} [M(CO)_5\{o\text{-}\overline{NHCH{=}C(PR_3)(C}_6H_4)\}]^+ \quad (1)$$
$$E_{\frac{1}{2}}^{ox}\ (\text{or } E_{p/2}^{ox}) = 0.65\text{–}0.55\ V \qquad E_{\frac{1}{2}}^{ox}\ (\text{or } E_{p/2}^{ox}) = 1.1\text{–}0.9\ V$$

such reversiblity was not observed in the case of the protonated carbene complexes which did not regenerate the parent carbene species on addition of base. As expected, the oxidation potentials of the protonated carbene or protonated indole complexes occur at considerably higher values (1.1–0.9 V) than those of the parent non-protonated compounds (0.9–0.5 V), but they still lie below the values exhibited by the starting isocyanide complexes (1.3–1.1 V), thus indicating that the phosphonium-functionalized isocyanide ligands behave as stronger net electron acceptors (or weaker net electron donors) than the protonated carbene or the protonated indole ligands.

Table 4 Estimated ligand parameters P_L and E_L for the phosphonium-functionalized isocyanides $CNC_6H_4CH_2PR_3{}^+\text{-}o$ and derived carbenes $\overline{CNHC_6H_4C}(PR_3)$, indoles $\overline{N{=}CHC(PR_3)(C}_6H_4)$ and protonated ligands

Ligand type	PR_3	$P_L{}^a$/V	$E_L{}^b$/V *vs* NHE
Isocyanide	PMe_3	−0.36[c]	0.43[d]
	$PPh_2(CH_2Ph)$	−0.30[c]	0.48[e]
	PPh_3	−0.28[f,g]	0.50[h]
Carbene	PMe_3	−0.87[c]	−0.01
	$PPh_2(CH_2Ph)$	−0.82[c]	0.03
	PPh_3	−0.79[g]	0.06
Indole	PMe_3	−0.99[f]	−0.11
	$PPh_2(CH_2Ph)$	−0.92[c]	−0.05
	PPh_3	−1.0[f]	−0.14
Protonated carbene	PMe_3	−0.60[c]	0.22
	$PPh_2(CH_2Ph)$	−0.51[g]	0.30
	PPh_3	−0.51[g]	0.30
Protonated indole	PMe_3	−0.44[f]	0.36
	$PPh_2(CH_2Ph)$	−0.62[c]	0.20
	PPh_3	−0.59[f]	0.23

[a] In V ± 0.02 [for the definition of P_L, see equation (2) or ref. 7]. [b] In V ± 0.02 *vs.* NHE (for the definition, see the text or ref. 8; estimated from equation (8). [c] Estimated by definition of P_L [equation (2)]. [d] A correction term (y) of 0.19 V has been estimated for the ligand at the $Cr(CO)_5$ binding centre (see text). [e] A correction term (y) of 0.25 V has been estimated for the ligand at the $Cr(CO)_5$ binding centre (see text). [f] Estimated from equation (5). [g] Estimated from equation (6). [h] A correction term (y) of 0.27 V has been estimated for the ligand at the $Cr(CO)_5$ binding centre (see text).

Estimate of the Electrochemical Ligand (P_L) *and Metal Centre* (β) *Parameters*.—The ligand parameter P_L has been defined[7] as in equation (2) and considered as a measure of the net electron σ

$$P_L = E_{\frac{1}{2}}^{ox}[Cr(CO)_5L] - E_{\frac{1}{2}}^{ox}[Cr(CO)_6] \qquad (2)$$

donor minus π acceptor ability of a ligand: the greater is the net electron-donor character of a ligand, the lower (usually more negative) is its P_L value. From this definition and taking into consideration our measured values of the oxidation potential for the present chromium complexes, as well as the known[24] value ($E_{\frac{1}{2}}^{ox}$ = 1.50 V) for $[Cr(CO)_6]$, we have estimated P_L for the following ligands (see Table 4): isocyanides $CNC_6H_4CH_2PR_3{}^+\text{-}o$ [$PR_3 = PMe_3$, $P_L = -0.36$; $PR_3 = PPh_2(CH_2Ph)$, $P_L = -0.30$ V], carbenes $\overline{CNHC_6H_4C}[PR_3)$ [$PR_3 = PMe_3$, $P_L = -0.87$; $PR_3 = PPh_2(CH_2Ph)$, $P_L = -0.82$ V], indole $\overline{N{=}CHC[PPh_2(CH_2Ph)](C}_6H_4)$ ($P_L = -0.92$ V), protonated carbene ($PR_3 = PMe_3$, $P_L = -0.60$ V) and protonated indole [$PR_3 = PPh_2(CH_2Ph)$, $P_L = -0.62$ V]. Moreover, the P_L values of the other ligands in this study have also been estimated as follows, although their complexes with $Cr(CO)_5$ were not available. For this purpose, we have considered the accessible analogous complexes with $Mo(CO)_5$ or $W(CO)_5$ and the expected corresponding linear dependences of the oxidation potential on P_L {[equation (3)], where E_S and β are the

$$E_{\frac{1}{2}}^{ox}[M_SL] = E_S + \beta P_L \qquad (3)$$

$$E_S = E_{\frac{1}{2}}^{ox}[M_S(CO)] \qquad (4)$$

electron-richness and the polarizability of the corresponding binding metal site M_S, the former being defined as $E_{\frac{1}{2}}^{ox}$ of the carbonyl complex with such a site [equation (4)]}.[7] However,

Table 5 The $E_{p/2}^{ox}$ (or $E_{\frac{1}{2}}^{ox}$)[a] and P_L data plotted in Figs. 2 and 3

L	$E_{p/2}^{ox}(E_{\frac{1}{2}}^{ox})$/V $[Mo(CO)_5L]$	 $[W(CO)_5L]$	P_L/V
CO	(1.50)[24]	(1.50)[24]	0[24]
$CNCH_2PPh_2(CH_2Ph)^+$	1.13[b]	1.24[b]	−0.30[b]
Protonated $CNHC_6H_4C(PMe_3)$	—	(0.90)[b]	−0.60[b]
$CNHC_6H_4C[PPh_2(CH_2Ph)]$	—	0.70[b]	−0.82[b]
$CNHC_6H_4C(PMe_3)$	—	0.77[b]	−0.87[b]
$N{=}CHC[PPh_2(CH_2Ph)](C_6H_4)$	0.55[b]	—	−0.92[b]
I	0.49[25]	0.44[25]	−1.15[7]
Br	0.46[25]	0.44[25]	−1.17[7]
Cl	0.44[25]	0.51[25]	−1.19[7]

[a] In V *vs.* SCE with $E_{\frac{1}{2}}^{ox}$ values in parentheses. [b] This work.

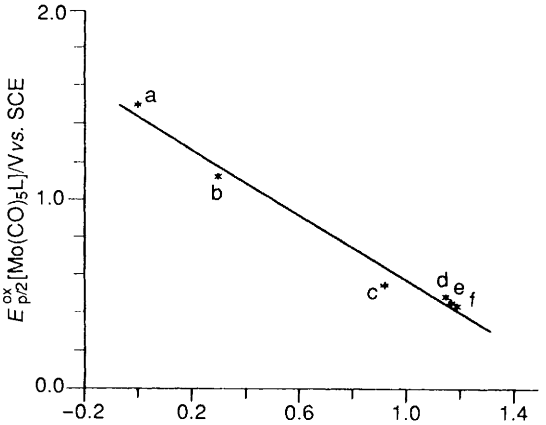


Fig. 2 Plot of $E_{\frac{1}{2}}^{ox}$ (or $E_{p/2}^{ox}$) *versus* P_L for the complexes $[Mo(CO)_5L]$ {L = CO (a), $CNC_6H_4CH_2PPh_2(CH_2Ph)^+$ (b), $N{=}CHC[PPh_2(CH_2Ph)](C_6H_4)$ (c), I (d), Br (e) or Cl (f)}. Estimate of β(slope) for $Mo(CO)_5$ [see equation (5)]

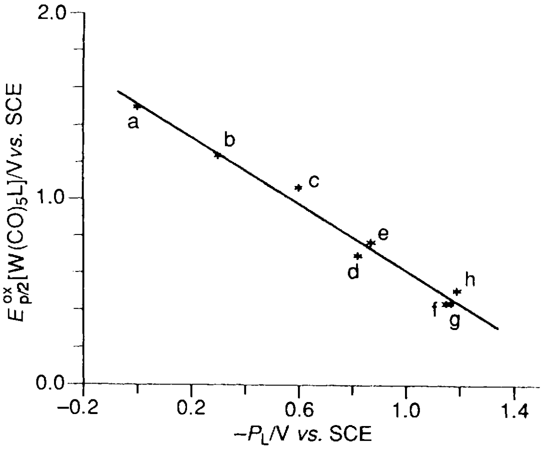


Fig. 3 Plot of $E_{\frac{1}{2}}^{ox}$ (or $E_{p/2}^{ox}$) *versus* P_L for the complexes $[W(CO)_5L]$ {L = CO (a), $CNC_6H_4CH_2PPh_2(CH_2Ph)^+$ (b), protonated $CNHC_6H_4C(PMe_3)$ (c), $CNHC_6H_4C[PPh_2(CH_2Ph)]$ (d), $CNHC_6H_4C(PMe_3)$ (e), I (f), Br (g) or Cl (h)}. Estimate of β(slope) for $W(CO)_5$ [see equation (6)]

although E_S is known for these molybdenum and tungsten sites since $E_{\frac{1}{2}}^{ox}[M(CO)_6] = 1.50$ V (M = Cr, Mo or W),[24] the polarizability (β) has not been reported for such metal centres. Therefore we have estimated this parameter by plotting (Figs. 2 and 3) the oxidation potentials ($E_{\frac{1}{2}}^{ox}$ or $E_{p/2}^{ox}$) of the members of each series of the complexes $[M(CO)_5L]$ (M = Mo or W) *versus* the corresponding P_L values for these cases where they were known (see Table 5).

The linear plots obtained are expressed by equations (5) and (6) (correlation coefficient 0.99). Their slopes provide β of 0.86

$$E_{\frac{1}{2}}^{ox}[Mo(CO)_5L] = 1.44 + 0.86P_L \qquad (5)$$

$$E_{\frac{1}{2}}^{ox}[W(CO)_5L] = 1.52 + 0.90P_L \qquad (6)$$

and 0.90 for $Mo(CO)_5$ or $W(CO)_5$, respectively. In addition, from such expressions, the P_L values have been estimated for the following ligands (see Table 4), by taking also into account the oxidation potentials, measured in this study, of their complexes with $M(CO)_5$ (M = Mo or W): $CNC_6H_4CH_2PPh_3{}^+$-*o* [$P_L = -0.28$ V, from equations (5) and (6)]: $CNHC_6H_4C(PPh_3)$ [−0.79 V, from equation (6)]; $N{=}CHC(PMe_3)(C_6H_4)$ [−0.99 V from equation (5)]; $N{=}C(H)C(PPh_3)(C_6H_4)$ [−1.0 V from equation (5)]; protonated $CNHC_6H_4C[PPh_2(CH_2Ph)]$ [−0.51 V from equation (6)]; protonated $CNHC_6H_4C(PPh_3)$ [−0.51 V from equation (6)]; $NHCH{=}C(PMe_3)(C_6H_4)$ [−0.44 V from equation (5)] and $NHCH{=}C(PPh_3)(C_6H_4)$ [−0.59 V from equation (5)].

As expected from the above discussion, the phosphonium-functionalized isocyanides present P_L values (−0.36 to −0.28 V) only marginally higher than those of other non-functionalized aromatic isocyanides (*e.g.* −0.40 to −0.38 V for CNC_6H_4X, where X = H, Me or OMe),[5a] as a result of the long distance of the phosphonium group from the metal, although they appear to reflect the electronic properties of this group. Moreover, the carbene ligands behave as much stronger net electron donors (P_L −0.87 to −0.79 V), even slightly stronger than other related aminocarbenes such as C(NRR′)Y (R,R′ or Y = H, alkyl, aryl or a related group) for which we can estimate P_L values in the range −0.80 to −0.75 V (see above); they appear to present net electron-donor abilities close to those of the anionic ligands NCS^- or $CF_3CO_2^-$ (P_L −0.88 or −0.78 V, respectively[7]).

Indoles are even stronger net electron donors with P_L values in the range −1.0 to −0.92 V which includes that of the CN^- ligand ($P_L = -1.00$ V[7]); they also have a net electron-releasing ability which is much greater than those exhibited by other N-donor ligands such as NCMe ($P_L = -0.58$ V[7]), pyridine ($P_L = -0.59$ V[7]) or even NH_3 ($P_L = -0.77$ V[10]). However, both the protonated indoles and the protonated carbenes are much weaker net electron donors and the range of their P_L values (−0.44 to *ca.* −0.6 V) includes those for NCMe, pyridine or thf (−0.58, −0.59 and *ca.* −0.6 V, respectively[7]).

Estimate of the Electrochemical Ligand Parameter E_L.—

Another electrochemical ligand parameter, E_L, has been proposed recently[8] to generate a series which may be used to predict the redox potential of complexes by assuming an additive contribution of all their ligands. The empirically derived relationship can assume the form (7) expressed in volts

$$E^{ox} = S_M(\Sigma E_L) + I_M \qquad (7)$$

vs. the normal hydrogen electrode (NHE), where S_M and I_M depend upon the metal and redox couple, the spin state and stereochemistry. Moreover, the linear relationship (8) has been

$$P_L = 1.17E_L - 0.86 \qquad (8)$$

experimentally observed[8] (for a considerable number of ligands, but not for CO) between E_L and P_L, thus allowing us to estimate the former (Table 4) from knowledge of the latter. Comparisons with other ligands with known[8] E_L values can then be made, in a similar way to that mentioned above on the basis of P_L; related conclusions can be reached, although not entirely identical in view of possible deviations from equation (8). Hence, *e.g.* the phosphonium-functionalized isocyanides present E_L values (0.50–0.43 V) somewhat higher than those of related non-functionalized aryl isocyanides (0.41–0.36 V[8]), whereas the carbene ligands (E_L 0.06 to −0.01 V) are comparable with cyanide (E_L = 0.02 V[8]), and the indoles (E_L = −0.05 to −0.14 V) with SCN^- (−0.06 V[8]) and $CF_3CO_2^-$ (−0.15 V[8]). Both carbenes and indoles are better net electron donors than, *e.g.*, pyridine (E_L = 0.25 V[8]), butyl- or isopropyl-amine (E_L = 0.13 or 0.05 V, respectively[8]), imidazole (0.12 V[8]) or even ammonia (0.07 V[8]). However, the protonated carbenes (E_L = 0.30–0.22 V) and the protonated indoles (E_L = 0.36–0.20 V) are comparable with acetonitrile (E_L = 0.34 V[8]), some isocyanides (*e.g.* CNC_6H_{11}, E_L = 0.32 V[8]) or pyridine (0.25 V[8]).

However, for ligands with an extensive π influence on the energy of the highest occupied molecular orbital (HOMO) (CO or isocyanides) the need for the introduction of corrections to E_L has been recognized,[8] by replacing equation (7) by (9)

$$E^{ox} = S_M(\Sigma E_L + mx + m'y) + I_M \qquad (9)$$

where m and m' are the numbers of ligands which interact directly with the HOMO (CO and CNR) and x and y are the corresponding corrections. Their values have been reported[8] for CO and for some alkyl or aryl isocyanides ligating $Cr(CO)_5$, but are still unknown for the analogous complexes of Mo or W.

By applying equation (9) to our $Cr(CO)_5$ isocyanide complexes, taking into account the known[8] values of S_M (0.52), I_M (−1.75 V *vs.* NHE) and x (0.15 for CO), and assuming that three CO ligands (m = 3) and one isocyanide ligand (m' = 1) interact directly with the HOMO, we have estimated the correction term (y) for the ligating isocyanides $CNC_6H_4CH_2PR_3{}^+$-*o* [y = 0.19 ($PR_3 = PMe_3$), 0.25 ($PR_3 = PPh_2(CH_2Ph)$) or 0.27 V ($PR_3 = PPh_3$)]. These values are comparable with that reported[8] for CNPh (0.19 V) at the same chromium site and appear to increase with the π acceptance of the phosphonium group in accord with the expected dominant role of π effects on such a correction.

We could also consider the possibility of estimating S_M and I_M, which have not yet been reported, for the $W(CO)_5$ metal site, through the application of equation (7) or (9). However, such an attempt appears to be premature in view of the narrow range of ΣE_L provided by this study for the complexes with that metal centre, as well as of the unavailability of the x and y corrections for such a site.

Nevertheless, this study allowed, for the first time, to estimate the P_L and E_L electrochemical ligand parameters for phosphonium-functionalized isocyanides and derived carbene, indole and their corresponding protonated ligands, thus providing an insight into their net electron-donor properties which have been compared with those of related ligands. The polarizability β has also been estimated for the metal centres $M(CO)_5$ (M = Mo or W). Cyclic voltammetry was also shown to provide a convenient method to monitor the interconversion of these types of species by following their reactions with base or acid.

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