Synthesis of Cationic Carbonyl Cyclopentadienyl Complexes of Molybdenum and Tungsten, and *X*-Ray Crystal Structure of (Acetone hydrazone)-tricarbonyl(η-cyclopentadienyl)tungsten Hexafluorophosphate

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Substitution of the hydrazine ligand in $[Mo(\eta\text{-}C_5H_5)(CO)_3(N_2H_4)]Cl$ with a range of commonly used tertiary phosphine and phosphite ligands (L) has provided a new high-yield route to $[Mo(\eta\text{-}C_5H_5)(CO)_3L]^+$ cations for the majority, but not all, of the ligands used. With phosphonites, phosphinites, and smaller phosphines there is a competing reaction to give $[Mo(\eta\text{-}C_5H_5)(CO)_2L_2]^+$ cations. Reaction of $[W(\eta\text{-}C_5H_5)(CO)_3(N_2H_4)]Cl$ with PPh_3 and $PMePh_2$ gives $[W(\eta\text{-}C_5H_5)(CO)_3L]^+$ (L = PPh_3 or $PMePh_2$) and $[W(\eta\text{-}C_5H_5)(NCO)(CO)_2(PPh_3)]$, depending on the reaction conditions. The complexes $[M(\eta\text{-}C_5H_5)(CO)_3(N_2H_4)]Cl$ (M = Mo or W) react with acetone to give the respective hydrazone cations $[M(\eta\text{-}C_5H_5)(CO)_3(NH_2NCMe_2)]^+$, which are thermodynamically more stable than the hydrazine precursors; $[Mo(\eta\text{-}C_5H_5)(CO)_3(NH_2NCMe_2)]^+$ is converted into $[Mo(\eta\text{-}C_5H_5)(CO)_2(solvent)_2]^+$ in polar solvents at room temperature. The crystal and molecular structure of $[W(\eta\text{-}C_5H_5)(CO)_3(NH_2NCMe_2)][PF_6]$ has been determined from three-dimensional *X*-ray data collected by counter methods. The structure has been refined by full-matrix least-squares techniques to a final *R* (on *F*) of 0.030, based on 2 141 reflections. The complex crystallises in the triclinic space group $P\bar{1}$ with two molecules in a cell of dimensions a = 10.81(2), b = 9.74(2), c = 8.47(2) Å, α = 113.3(1), β = 96.0(1), and γ = 95.1(1)°. The tungsten atom is formally seven co-ordinate and the complex is best described as possessing the ' piano-stool ' geometry. The major feature is the mode of bonding of the hydrazone ligand, which is shown to occur through the amino-nitrogen atom, in contradiction to current theories on the bonding of hydrazones to transition metals. Possible factors influencing the relative stability of amino- or imino-nitrogen bonding are discussed.

SUBSTITUTION reactions of the tricarbonyl(η-cyclopentadienyl)-molybdenum and -tungsten halides with tertiary and ditertiary phosphorus ligands (L) have been the subject of several studies,[1-7] although no clear trend has emerged as to the factors determining the formation of neutral or cationic derivatives. In particular, no reliable routes to the monosubstituted cations $[M(\eta\text{-}C_5H_5)(CO)_3L]^+$ have been devised, although $[M(\eta\text{-}C_5H_5)(CO)_3(PPh_3)]^+$ (M = Mo or W) have been shown [8] to undergo an almost [9] unique reaction in co-ordination chemistry, *viz.* sodium tetrahydroborate reduction of one bonded carbonyl to a methyl group. Recently the closely related acyl complex $[Mo(\eta\text{-}C_5H_5)(COMe)(CO)_2(PPh_3)]$ has also been shown [10] to undergo preferential acyl-group reduction with B_2H_6–C_6H_6, giving the ethyl derivative $[Mo(\eta\text{-}C_5H_5)Et(CO)_2(PPh_3)]$. Since $[Mo(\eta\text{-}C_5H_5)Me(CO)_2(PPh_3)]$ and $[Mo(\eta\text{-}C_5H_5)(COMe)(CO)_2(PPh_3)]$ are related by a carbonyl insertion–elimination reaction, it seems feasible that this system can provide a means of studying the conversion of co-ordinated carbon monoxide into an ethyl group. Current interest in the formation of hydrocarbons from carbon monoxide has thus enhanced the status of the $[M(\eta\text{-}C_5H_5)(CO)_3L]^+$ (M = Mo or W) cations and prompted us to study their formation with a range of tertiary phosphorus ligands (L). Application of standard preparative methods has thus far been of only limited success and these cations have been characterised for very few ligands.[1-3] The most successful route [2] has been *via* reaction of $[M(\eta\text{-}C_5H_5)Cl(CO)_3]$ with $AlCl_3$ in the presence of L, although this method produced mixtures of $[M(\eta\text{-}C_5H_5)(CO)_3L]^+$ and $[M(\eta\text{-}C_5H_5)(CO)_2L_2]^+$ and the procedure of product isolation made the method suitable only for fairly stable cations.

We have now utilised the ready replacement [11] of co-ordinated hydrazine in the known [12] unstable complexes $[M(\eta\text{-}C_5H_5)(CO)_3(N_2H_4)]Cl$ (M = Mo or W) to provide a more reliable route to the $[M(\eta\text{-}C_5H_5)(CO)_3L]^+$ cations. Direct reaction of $[M(\eta\text{-}C_5H_5)(CO)_3(N_2H_4)]Cl$ with acetone has also yielded unusual acetone hydrazone cations $[M(\eta\text{-}C_5H_5)(CO)_3(NH_2NCMe_2)]^+$ (M = Mo or W), which are more stable than the hydrazine precursors. The *X*-ray crystal structure of $[W(\eta\text{-}C_5H_5)(CO)_3(NH_2NCMe_2)][PF_6]$ has shown that the hydrazone ligand is bonded through the amino-nitrogen, which is contrary to current theories on metal–hydrazone bonding.[13-15]

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EXPERIMENTAL

Starting Materials.—The complexes $[M(\eta\text{-}C_5H_5)Cl(CO)_3]$ (M = Mo or W) were prepared as described previously [16] from the respective hexacarbonyls. All the ligands were obtained commercially and were not further purified. All the operations were carried out under an inert atmosphere and the majority of the cationic complexes were light-sensitive over a period of days.

Preparation of Complexes.—*(Acetone hydrazone)tricarbonyl(η-cyclopentadienyl)molybdenum hexafluorophosphate*, $[Mo(\eta\text{-}C_5H_5)(CO)_3(NH_2NCMe_2)][PF_6]$. A solution of anhydrous hydrazine (0.68 g, 21.3 mmol) in dichloromethane (5 cm^3) was added dropwise to a stirred solution of $[Mo(\eta\text{-}C_5H_5)Cl(CO)_3]$ (1.0 g, 3.6 mmol) in dichloromethane (20 cm^3) at 0 °C. The red colour rapidly disappeared and $[Mo(\eta\text{-}C_5H_5)(CO)_3(N_2H_4)]Cl$ [12] was deposited as a yellow solid. The reaction mixture was kept at 0 °C and after 5 min acetone (10 cm^3) was added dropwise. The solution was allowed to warm to room temperature and filtered into a solution of $[NH_4][PF_6]$ (0.70 g, 4.3 mmol) in ethanol (15 cm^3). The volume was reduced to 10 cm^3 under reduced pressure and crystallisation was induced by addition of diethyl ether. The required product was obtained as orange prisms (0.64 g, 39%) and could be recrystallised from dichloromethane–ethanol. The complex $[W(\eta\text{-}C_5H_5)(CO)_3(NH_2NCMe_2)][PF_6]$ was similarly prepared from $[W(\eta\text{-}C_5H_5)Cl(CO)_3]$ as red prisms in 48% yield.

TABLE 1

Physical data for cyclopentadienyl carbonyl complexes of molybdenum and tungsten

Complex	M.p. [a] (θ_c/°C)	Λ [b] / S cm^2 mol^{-1}	Analysis (%) [c] C	H	N	ν(CO) [d] / cm^{-1}	^{1}H N.m.r. (τ) [e] C_5H_5	Other
$[Mo(\eta\text{-}C_5H_5)(CO)_3(NH_2NCMe_2)][PF_6]$	97—99	139	28.7(28.6)	2.65(2.85)	6.1(6.05)	2 062s, 1 967s,br	4.05(s)	3.72(m)(NH_2), 8.03(s)(Me), 8.08(s)(Me)
$[W(\eta\text{-}C_5H_5)(CO)_3(NH_2NCMe_2)][PF_6]$	122—125	129	24.05(24.0)	2.2(2.4)	5.2(5.1)	2 053s, 1 951s,br	3.92(s)	3.42(m)(NH_2), 7.98(s)(Me), 8.08(s)(Me)
$[Mo(\eta\text{-}C_5H_5)(CO)_3(PMePh_2)][PF_6]$	206—208	134	42.85(42.75)	2.9(3.05)		2 055s, 1 962s,br	3.99(s)	7.45(d)[*J*(P–H) 9.8]
$[W(\eta\text{-}C_5H_5)(CO)_3(PMePh_2)][PF_6]$	218—224	128	37.2(37.2)	2.6(2.65)		2 053s, 1 974sh, 1 948s,br	3.87(s)	7.35(d)[*J*(P–H) 9.8] 7.76(m)
$[Mo(\eta\text{-}C_5H_5)(CO)_3(PEt_3)][PF_6]$	226—229	148	33.25(33.1)	4.05(3.95)		2 053s, 1 982(sh), 1 958s,br	3.90(s)	8.71(t)[*J*(H–H 7.7], 8.89(t) [*J*(H–H) 7.7]
$[Mo(\eta\text{-}C_5H_5)(CO)_3\{P(OMe)_3\}][PF_6]$	189—194	157	25.8(25.7)	2.8(2.75)		2 070s, 1 998(sh), 1 976s,br	3.89(s)	6.08(d)[*J*(P–H) 11.8]
$[Mo(\eta\text{-}C_5H_5)(CO)_2(PMe_2Ph)_2][PF_6]$	221—223	143	43.6(43.3)	4.45(4.25)		1 963m, 1 881s	4.57(t) [f]	7.86(d)[*J*(P–H) 9.8]
$[Mo(\eta\text{-}C_5H_5)(CO)_2(NCMe)_2][BPh_4]$	128—129	116	68.25(68.0)	5.05(5.05)	4.5(4.55)	1 995s, 1 909s [g]	4.24(s)	7.58(s) [h]
$[W(\eta\text{-}C_5H_5)(NCO)(CO)_2(PPh_3)]$	211—213	4.9	51.0(51.25)	3.2(3.3)	2.4(2.3)	2 241s,[i] 1 950s, 1 863s	4.30(s)	

[a] All the complexes melted with decomposition. [b] 0.01 mol in acetone solution. [c] Calculated values are given in parentheses. [d] Recorded in acetone solution; s = strong, m = medium, sh = shoulder, and br = broad. [e] Recorded in $(CD_3)_2CO$ solution. *J* values (in Hz) are given in square brackets. [f] *J*(P–H) *ca.* 1.0 Hz. [g] Infrared (C≡N) bands at 2 318 and 2 284 cm^{-1} in Nujol. [h] In CD_3NO_2 solution. Spectrum indicated exchange of MeCN ligands with solvent. [i] ν(NCO).

Tricarbonyl(η-cyclopentadienyl)(methyldiphenylphosphine)molybdenum hexafluorophosphate, $[Mo(\eta\text{-}C_5H_5)(CO)_3(PMePh_2)][PF_6]$. A precipitate of $[Mo(\eta\text{-}C_5H_5)(CO)_3(N_2H_4)]Cl$ in dichloromethane (25 cm^3) was prepared using the quantities of anhydrous hydrazine and $[Mo(\eta\text{-}C_5H_5)Cl(CO)_3]$ described above. After 5 min at 0 °C a solution of methyldiphenylphosphine (0.74 g, 3.7 mmol) in acetone (10 cm^3) was added dropwise. The reaction solution was warmed to room temperature, stirred for 15 min, and filtered into a solution of $[NH_4][PF_6]$ (0.70 g, 4.3 mmol) in ethanol (10 cm^3). The volume was reduced to 10 cm^3 under reduced pressure and precipitation was induced by addition of diethyl ether (30 cm^3). Recrystallisation from dichloromethane–ethanol gave the required complex as yellow needles (1.28 g, 61%).

Similarly prepared were $[Mo(\eta\text{-}C_5H_5)(CO)_3(PEt_3)][PF_6]$ as yellow microcrystals in 52% yield, $[Mo(\eta\text{-}C_5H_5)(CO)_3\{P(OMe)_3\}][PF_6]$ as yellow needles in 47% yield, $[Mo(\eta\text{-}C_5H_5)(CO)_2(PMe_2Ph)_2][PF_6]$ as yellow plates in 44% yield, and the known [2] complex $[Mo(\eta\text{-}C_5H_5)(CO)_3(PPh_3)][PF_6]$ in 68% yield. Also prepared by analogous procedures from $[W(\eta\text{-}C_5H_5)Cl(CO)_3]$ were $[W(\eta\text{-}C_5H_5)(CO)_3(PMePh_2)][PF_6]$ as yellow prisms in 66% yield and the known [2] complex $[W(\eta\text{-}C_5H_5)(CO)_3(PPh_3)][PF_6]$ in 59% yield.

Dicarbonyl(η-cyclopentadienyl)isocyanato(triphenylphosphine)tungsten, $[W(\eta\text{-}C_5H_5)(NCO)(CO)_2(PPh_3)]$. This complex was prepared by slightly modifying the reaction procedure described for $[W(\eta\text{-}C_5H_5)(CO)_3(PPh_3)][PF_6]$ above. A suspension of $[W(\eta\text{-}C_5H_5)(CO)_3(N_2H_4)]Cl$ in dichloromethane was treated with 1 mol equivalent of triphenylphosphine in dichloromethane solution at ±10 °C. After 10 min, addition of excess of acetone and work-up of the reaction solution as described above produced a mixture of $[W(\eta\text{-}C_5H_5)(CO)_3(NH_2NCMe_2)][PF_6]$ and the required product. These could be separated by fractional crystallisation using dichloromethane–ethanol. The required complex crystallised as red prisms in rather variable yield (optimum 18%).

Bis(acetonitrile)dicarbonyl(η-cyclopentadienyl)molybdenum tetraphenylborate, $[Mo(\eta\text{-}C_5H_5)(CO)_2(NCMe)_2][BPh_4]$. This complex was prepared by allowing a solution of $[Mo(\eta\text{-}C_5H_5)(CO)_3(NH_2NCMe_2)][PF_6]$ (0.4 g, 0.86 mmol) in methyl cyanide (15 cm^3) to stand at room temperature under an inert atmosphere for 24 h. Addition of sodium tetraphenylborate (0.31 g, 0.90 mmol) in ethanol (15 cm^3) and concentration of the solution gave a precipitate which could be recrystallised from dichloromethane–ethanol as orange microcrystals (0.34 g, 64%).

Melting points were obtained on a Kofler hot-stage apparatus and conductivities were measured in acetone solution on a Van Waters and Rogers model 31 conductivity bridge. Infrared spectra were recorded using a Perkin-Elmer model 457 grating spectrophotometer, and ^{1}H n.m.r. spectra with Varian A-60A and HA-100 instruments. Elemental analyses were carried out in this laboratory.

Crystal Data.—$[W(\eta\text{-}C_5H_5)(CO)_3(NH_2NCMe_2)][PF_6]$, $M = 550.1$, Triclinic, $a = 10.81(2)$, $b = 9.74(2)$, $c = 8.47(2)$ Å, $\alpha = 113.3(1)$, $\beta = 96.0(1)$, $\gamma = 95.1(1)°$, $U = 806$ Å^3, $D_c = 2.27$ g cm^{-3}, $Z = 2$, $D_m = 2.29$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 77.8$ cm^{-1}, space group $P\bar{1}$. The dimensions of the crystal were 0.12 × 0.12 × 0.16 mm.

Unit-cell dimensions were obtained from preliminary oscillation and Weissenberg photographs which revealed no symmetry elements, from which the crystal system was inferred to be triclinic. Final cell dimensions were calculated from a least-squares refinement of the angular settings

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of 24 reflections. Reflection intensities were measured on the Philips PW1100 diffractometer at the National Physical Research Laboratory, Council for Scientific and Industrial Research, by the ω—2θ scan technique with Mo-K_α radiation (λ 0.710 7 Å) between θ 3 and 23°. Of a total of 2 244 independent reflections, 2 141 were observed with $I > 1.65\sigma(I)$. The intensities of three reference reflections were measured every hour and showed variations of less than $\pm 3\%$, so that no decomposition corrections were applied. The recorded intensities were corrected for background, Lorentz, and polarisation effects and for absorption (μr 0.64).

Structure Solution and Refinement.—The choice of the triclinic space group $P\bar{1}$ was confirmed by successful refinement. The position of the tungsten atom was obtained from a three-dimensional Patterson function and the 23 remaining non-hydrogen atoms were identified from electron-density maps and least-squares calculations. The atomic scattering factors used for all the atoms were those obtained by Cromer and Mann.[17] The effects of anomalous dispersion were included in the calculations for tungsten and phosphorus atoms.[18] Full-matrix least-squares refinement of positional, isotropic thermal (C and N), and anisotropic thermal (W, P, F, and O) parameters led to convergence with $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.030$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}} = 0.036$, using unit weights. No attempt was made to locate the hydrogen atoms on the final difference map which did not show any significant peaks. All the computing was performed on an IBM 360/65 computer, using the '*X*-RAY' program package[19] and the ORTEP plotting program.[20] The final atomic parameters with their standard deviations are listed in Table 2. Tables of observed and calculated structure factors and atomic thermal parameters are listed in Supplementary Publication No. SUP 22241 (15 pp.).*

TABLE 2

Atomic parameters with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
W	0.199 29(3)	0.328 29(4)	0.171 61(4)
C(1)	0.053 4(9)	0.318 9(10)	−0.005 0(12)
C(2)	0.101 4(9)	0.488 2(10)	0.313 7(12)
C(3)	0.320 3(9)	0.520 3(11)	0.257 5(12)
O(1)	−0.032 4(6)	0.308 2(9)	−0.101 1(9)
O(2)	0.047 4(7)	0.579 3(7)	0.393 2(9)
O(3)	0.391 8(7)	0.627 8(8)	0.319 6(9)
N(1)	0.292 5(7)	0.285 9(8)	−0.067 7(9)
N(2)	0.218 2(7)	0.163 5(8)	−0.223 0(10)
C(4)	0.277 6(8)	0.064 5(10)	−0.321 0(11)
C(5)	0.418 0(11)	0.059 9(13)	−0.296 9(15)
C(6)	0.200 9(10)	−0.061 0(12)	−0.479 4(14)
C(7)	0.160 3(9)	0.075 3(11)	0.129 7(13)
C(8)	0.294 7(9)	0.116 7(11)	0.168 6(13)
C(9)	0.324 8(10)	0.234 1(12)	0.339 4(13)
C(10)	0.208 6(10)	0.266 8(12)	0.407 6(14)
C(11)	0.107 9(9)	0.171 1(11)	0.280 7(13)
P	0.678 4(2)	0.322 8(3)	0.146 1(3)
F(1)	0.653 0(8)	0.396 3(9)	0.338 7(8)
F(2)	0.701 7(6)	0.245 7(7)	−0.049 3(8)
F(3)	0.775 3(6)	0.467 0(7)	0.177 5(9)
F(4)	0.576 9(8)	0.179 8(8)	0.109 6(10)
F(5)	0.786 5(8)	0.243 6(9)	0.199 9(11)
F(6)	0.569 2(6)	0.399 5(9)	0.082 0(10)

RESULTS AND DISCUSSION

The known[12] thermally unstable complexes $[M(\eta\text{-}C_5H_5)(CO)_3(N_2H_4)]Cl$ (M = Mo or W) were prepared as yellow precipitates in dichloromethane and treated *in situ* with 1 mol equivalent of a tertiary phosphorus ligand dissolved in acetone solution. In this way all the excess of hydrazine present in the reaction solutions was converted into acetone azine, and the substituted molybdenum and tungsten cations could be isolated as the hexafluorophosphate salts after addition of ammonium hexafluorophosphate. An extensive series of ligands was tested during the molybdenum reactions and the method was shown to provide a reliable high-yield route to $[Mo(\eta\text{-}C_5H_5)(CO)_3L][PF_6]$ species for the majority of ligands used, although there were notable exceptions. Thus $[Mo(\eta\text{-}C_5H_5)(CO)_3L][PF_6]$ [L = PPh_3,[2] $PMePh_2$, PEt_3, $P(OEt)_3$, $P(OMe)_3$, or $P(OPh)_3$] were prepared in yields of 39—68%, with these ligands representing all the phosphites and the larger phosphine ligands used. With $PPh_2(OMe)$ and $PPh(OMe)_2$, equimolar mixtures of $[Mo(\eta\text{-}C_5H_5)(CO)_{4-x}L_x][PF_6]$ (x = 1 or 2) were formed and with PMe_2Ph the only isolable product was $[Mo(\eta\text{-}C_5H_5)(CO)_2(PMe_2Ph)_2][PF_6]$. The preferential formation of this disubstituted species for certain ligands is a feature which has been noted previously,[3,4] particularly during preparations of phosphine-substituted $[Mo(\eta\text{-}C_5H_5)(CO)_3L]^+$ cations using halide-abstraction techniques.[2] Their formation by the present method cannot readily be explained on the basis of either steric or electronic ligand effects, although it appears that the loss of the carbonyl ligand occurs simultaneously with the hydrazine-ligand replacement, since the complexes $[Mo(\eta\text{-}C_5H_5)(CO)_3L][PF_6]$ do not react further with ligands L under the conditions of the reaction or even in refluxing dichloromethane solutions.

The complexes $[Mo(\eta\text{-}C_5H_5)(CO)_3L][PF_6]$ [L = PPh_3,[2] $PMePh_2$, PEt_3, or $P(OMe)_3$] and $[Mo(\eta\text{-}C_5H_5)(CO)_2(PMe_2Ph)_2][PF_6]$ were fully characterised and the remaining molybdenum complexes were identified only from the characteristic carbonyl bands in their i.r. spectra. The analogous tungsten complexes $[W(\eta\text{-}C_5H_5)(CO)_3L][PF_6]$ (L = PPh_3 [2] or $PMePh_2$) were also prepared. All the cationic complexes are pale yellow and fairly stable in solution, but tend to be somewhat light-sensitive in the solid state. Infrared spectra of the monosubstituted complexes $[M(\eta\text{-}C_5H_5)(CO)_3L][PF_6]$ in acetone solution contained three ν(CO) bands, two of which were only partially resolved (see Table 1). The ^1H n.m.r. spectrum of $[Mo(\eta\text{-}C_5H_5)(CO)_3(PEt_3)][PF_6]$ (see Table 1) was unusually complex, containing a *ca.* 1 : 4 : 6 : 4 : 1 quintet for the phosphine methylene protons and two 1 : 2 : 1 triplets for the methyl protons. The quintet is consistent with coupling of the methylene protons with three protons of the adjacent methyl group

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

[17] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[18] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1968, vol. 3, p. 215.

[19] J. M. Stewart, G. J. Kruger, H. Ammon, C. H. Dickinson, and S. R. Hall, University of Maryland, Technical Report TR 192, version of June 1972.

[20] C. K. Johnson, Report ORNL TM 3794, Oak Ridge National Laboratories, Oak Ridge, Tennessee, 1965.

and one ^{31}P nucleus, both coupling constants being of the order of ±8 Hz. The two methyl triplets arise from coupling of the methyl protons to the ^{31}P nucleus in addition to the adjacent methylene protons, and the separation of the triplets establishes the magnitude of the J(P–H) (methyl) coupling as 18 Hz. The larger J(P–H) for the more remote methyl protons has been observed previously.[21,22]

Two isomeric forms, denoted lateral and diagonal,[23] are possible for $[Mo(\eta\text{-}C_5H_5)(CO)_2(PMe_2Ph)_2][PF_6]$ and the relative intensities of the two observed ν(CO) bands suggested that the complex exists as the diagonal isomer in solution, with the intensity of the asymmetric band (1 881 cm^{-1}) being approximately three times greater than that of the symmetric band (1 963 cm^{-1}).[24] The assignment was confirmed by the ^{1}H n.m.r. spectrum of the complex which contained the characteristic [4,25] triplet for the C_5H_5 protons and a single methyl doublet for the phosphine resonance [26] (see Table 1). The predominance of the diagonal isomer in solution may be rationalised on steric grounds.[27]

A second complex could be isolated from the reaction of $[W(\eta\text{-}C_5H_5)(CO)_3(N_2H_4)]Cl$ with PPh_3. When the ligand was added in the absence of acetone the reaction gave the neutral isocyanate complex $[W(\eta\text{-}C_5H_5)(NCO)(CO)_2(PPh_3)]$, having ν(NCO) at 2 241 cm^{-1}, in place of the previous cationic species. The two i.r. carbonyl bands of approximately equal intensity and the singlet resonance in the ^{1}H n.m.r. spectrum for the C_5H_5 protons characterised this complex as the lateral isomer in solution.[4] This is in agreement with the assignment made for the molybdenum analogue, $[Mo(\eta\text{-}C_5H_5)(NCO)(CO)_2(PPh_3)]$, which has been described previously.[28] The formation of an isocyanate ligand by hydrazine attack on a co-ordinated carbonyl is well known [29] and has been postulated to occur *via* intermediate formation of a carbamoyl complex.[30,31]

During a number of the reactions of $[Mo(\eta\text{-}C_5H_5)(CO)_3(N_2H_4)]Cl$ described above it was possible to isolate a very low yield of a deep red cationic complex as a by-product of the reaction. Treatment of the hydrazine salt with acetone at ±10 °C in the absence of other ligands and addition of $[NH_4][PF_6]$ produced a 39% yield of this complex which was characterised as the acetone hydrazone derivative, $[Mo(\eta\text{-}C_5H_5)(CO)_3(NH_2NCMe_2)][PF_6]$. The tungsten analogue could be similarly prepared in 48% yield. The only previously reported example of a Group 6 metal hydrazone complex is $[Cr(CO)_5(NH_2NCMe_2)]$.[32] The i.r. spectra of the hydrazone cations contained ν(C=N) bands at 1 661 (Mo) and 1 664 cm^{-1} (W) and the expected ν(CO) bands which were similar to those observed for the other $[M(\eta\text{-}C_5H_5)(CO)_3L]^+$ cations. The ^{1}H n.m.r. spectrum of $[W(\eta\text{-}C_5H_5)(CO)_3(NH_2NCMe_2)][PF_6]$ contained two methyl singlets of equal intensity, arising from the magnetically non-equivalent methyl groups on the acetone hydrazone ligand. The ^{1}H n.m.r. spectrum of the molybdenum analogue contained additional peaks which grew in intensity over a period of time. Analysis of the spectrum in either $(CD_3)_2CO$ or CD_3NO_2 solution indicated that a 20% conversion into a new complex took place soon after dissolving the complex and a 90% conversion was obtained after 24 h. An i.r. spectrum of the final solution contained carbonyl-stretching frequencies characteristic of a dicarbonyl species, although the complex could not be isolated. When $[Mo(\eta\text{-}C_5H_5)(CO)_3(NH_2NCMe_2)][PF_6]$ was dissolved in methyl cyanide it was possible after 24 h to isolate the solvolysed species, $[Mo(\eta\text{-}C_5H_5)(CO)_2(NCMe)_2]^+$, as the tetraphenylborate salt. The hexafluorophosphate analogue has been partially characterised previously.[2] Thus the hydrazone ligand is readily labilised in the molybdenum complex to give solvolysed species in polar solvents and the concomitant loss of the carbonyl group again demonstrates the tendency of the system to give an $[M(\eta\text{-}C_5H_5)(CO)_2L_2]^+$ derivative.

The greater stability of the hydrazone ligand, compared to hydrazine in $[M(\eta\text{-}C_5H_5)(CO)_3L]^+$ (M = Mo or W), both in the solid state and in solution, is surprising in view of the reduced basicity of the amino-nitrogen in the hydrazone.[33] The $[M(\eta\text{-}C_5H_5)(CO)_3(NH_2NCMe_2)][PF_6]$ complexes are not, as might be expected, intermediates in the formation of the $[M(\eta\text{-}C_5H_5)(CO)_3L]^+$ cations during reactions of $[M(\eta\text{-}C_5H_5)(CO)_3(N_2H_4)]Cl$ with ligands L in acetone solution. Thus, treatment of $[Mo(\eta\text{-}C_5H_5)(CO)_3(NH_2NCMe_2)][PF_6]$ with 1 mol equivalent of a tertiary phosphorus ligand L, at room temperature, gave only a $[Mo(\eta\text{-}C_5H_5)(CO)_2L_2][PF_6]$ derivative, probably *via* the solvolysed species, and hydrazone displacement in the tungsten analogue could only be effected after extended reflux in acetone, giving the dicarbonyl also.

Higher stability towards substitution of a hydrazone complex, compared to a corresponding hydrazine complex, has been observed previously in $[Ru(NH_2NCMe_2)_2\{P(OMe)_3\}_4][BPh_4]_2$,[34] and a crystal-structure determination showed the stability to arise from hydrogen bonding of the hydrazone ligand to the phosphite oxygen

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atoms. In order to determine whether a highly unusual hydrogen bond to a carbonyl oxygen atom is formed in the present hydrazone complexes we have determined the crystal structure of [W(η-C_5H_5)$(CO)_3$(NH_2NCMe_2)]-[PF_6].

TABLE 3

Bond lengths (Å) with estimated standard deviations in parentheses

W–N(1)	2.27(1)	C(7)–C(8)	1.44(1)
W–C(1)	2.03(1)	C(8)–C(9)	1.43(1)
W–C(2)	2.02(1)	C(9)–C(10)	1.45(2)
W–C(3)	2.01(1)	C(10)–C(11)	1.41(1)
W–C(7)	2.34(1)	C(11)–C(7)	1.46(1)
W–C(8)	2.38(1)	N(1)–N(2)	1.47(1)
W–C(9)	2.36(1)	N(2)–C(4)	1.27(1)
W–C(10)	2.30(1)	C(4)–C(5)	1.52(2)
W–C(11)	2.28(1)	C(4)–C(6)	1.51(1)
P–F(1)	1.57(1)	C(1)–O(1)	1.14(1)
P–F(2)	1.58(1)	C(2)–O(2)	1.13(1)
P–F(3)	1.59(1)	C(3)–O(3)	1.14(1)
P–F(4)	1.60(1)		
P–F(5)	1.58(1)		
P–F(6)	1.61(1)		

X-Ray Structure.—All the bond lengths and angles are shown in Tables 3 and 4, together with their standard deviations, and the numbering system of the molecule is given in the Figure. The crystal structure consists of discrete [W(η-C_5H_5)$(CO)_3$(NH_2NCMe_2)]$^+$ cations and [PF_6]$^-$ anions. The closest approach between the anionic fluorine and the cationic oxygen and nitrogen atoms is 3.0—3.1 Å. The molecular packing contains a number of close approaches between oxygen atoms which are within the same range (see Table 5). The [PF_6]$^-$ anion exhibits the usual high thermal motion of the fluorine atoms. The P–F bond distances are distributed between 1.57 and 1.61 Å and the F–P–F angles lie between 88 and 92°, and 177 and 179°.

TABLE 4

Bond angles (°) with estimated standard deviations in parentheses

N(1)–W–C(1)	78.2(4)	C(1)–W–C(2)	76.8(4)
N(1)–W–C(2)	135.0(4)	C(1)–W–C(3)	113.0(4)
N(1)–W–C(3)	80.2(3)	C(1)–W–C(7)	96.3(4)
N(1)–W–C(7)	96.2(3)	C(1)–W–C(8)	124.7(3)
N(1)–W–C(8)	82.2(4)	C(1)–W–C(9)	155.5(4)
N(1)–W–C(9)	104.9(3)	C(1)–W–C(10)	132.0(4)
N(1)–W–C(10)	140.0(4)	C(1)–W–C(11)	99.7(4)
N(1)–W–C(11)	132.8(3)	C(2)–W–C(3)	76.0(4)
C(3)–W–C(7)	148.7(4)	C(2)–W–C(7)	123.3(4)
C(3)–W–C(8)	113.7(4)	C(2)–W–C(8)	142.5(4)
C(3)–W–C(9)	91.4(4)	C(2)–W–C(9)	113.3(4)
C(3)–W–C(10)	103.4(4)	C(2)–W–C(10)	83.1(4)
C(3)–W–C(11)	138.6(4)	C(2)–W–C(11)	88.1(4)
C(7)–W–C(8)	35.3(3)	C(8)–W–C(9)	35.1(3)
C(7)–W–C(9)	59.3(3)	C(8)–W–C(10)	59.5(4)
C(7)–W–C(10)	60.1(3)	C(8)–W–C(11)	60.1(4)
C(7)–W–C(11)	36.8(3)	C(9)–W–C(10)	36.2(4)
C(10)–W–C(11)	35.9(3)	C(9)–W–C(11)	59.9(4)
W–C(1)–O(1)	176(1)	W–N(1)–N(2)	111.6(5)
W–C(2)–O(2)	179(1)	N(1)–N(2)–C(4)	117.0(7)
W–C(3)–O(3)	174(1)	N(2)–C(4)–C(5)	127.0(7)
C(7)–C(8)–C(9)	108.2(9)	N(2)–C(4)–C(6)	116.7(8)
C(8)–C(9)–C(10)	108.0(8)	C(5)–C(4)–C(6)	116.2(8)
C(9)–C(10)–C(11)	108.5(8)	F(1)–P–F(2)	178.8(6)
C(10)–C(11)–C(7)	108.0(9)	F(1)–P–F(3)	90.8(4)
C(11)–C(7)–C(8)	107.3(7)	F(1)–P–F(4)	90.0(4)
F(3)–P–F(4)	177.7(5)	F(1)–P–F(5)	90.9(5)
F(3)–P–F(5)	91.5(4)	F(1)–P–F(6)	91.7(5)
F(3)–P–F(6)	88.7(4)	F(2)–P–F(3)	90.4(4)
F(4)–P–F(5)	90.7(5)	F(2)–P–F(4)	88.8(4)
F(4)–P–F(6)	89.1(4)	F(2)–P–F(5)	89.2(4)
F(5)–P–F(6)	177.3(5)	F(2)–P–F(6)	88.2(4)

In the cation the tungsten atom is bonded to the cyclopentadienyl ring, the amino-nitrogen of the acetone hydrazone ligand, and three carbonyl groups. The cyclopentadienyl ring may be considered as a tridentate six-electron donor [35] and the co-ordination number is thus seven, although classification of the type of seven-co-ordination [36] is complicated by the five-fold symmetry of the ring. The complex is best described as possessing the ' piano-stool ' geometry,[34] which consists of a cube with the metal atom at the centre, the cyclopentadienyl ring in the plane of one face, and the four remaining ligands attached at the corners of the opposite face. In [W(η-C_5H_5)$(CO)_3$(NH_2NCMe_2)][PF_6] the dihedral angle between the planes of the cyclopentadienyl ring and the four basal ligands is 4°, compared to 3° for the closely related [W(η-C_5H_5)($GaMe_2$)$(CO)_3$].[37] This bonding

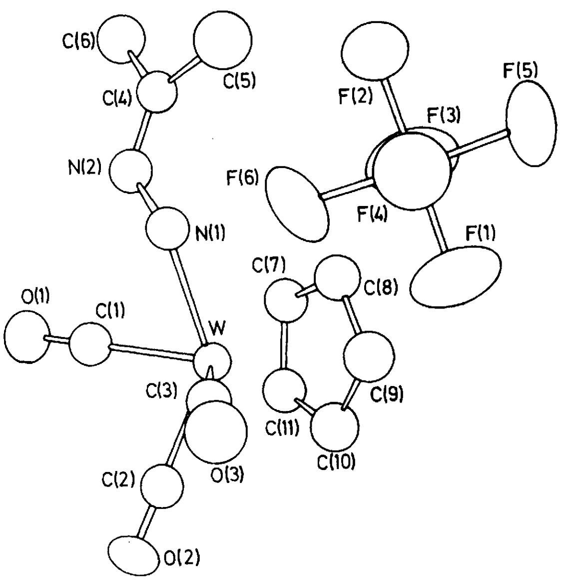

FIGURE The atom-numbering scheme for [W(η-C_5H_5)$(CO)_3$(NH_2NCMe_2)][PF_6]

TABLE 5

Some non-bonded and inter- and intra-molecular distances (Å) with estimated standard deviations in parentheses

F(4) ··· N(1)	3.69(1)	F(4) ··· C(8)	3.19(1)
F(6) ··· N(1)	3.05(1)	F(1) ··· O(1) *	3.00(1)
F(3) ··· N(1) *	3.02(1)	F(6) ··· O(3)	3.27(1)
O(1) ··· N(1)	3.53(1)	O(1) ··· O(1) *	3.41(1)
O(3) ··· N(1)	3.60(1)	O(2) ··· O(2) *	3.00(1)
		O(1) ··· O(2) *	3.07(1)

* These atoms are symmetry-related to those in Table 1.

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arrangement has only been observed previously in the complex $[\mathrm{Ru(NH_2NCMe_2)_2\{P(OMe)_3\}_4][BPh_4]_2}$.[34] In the present complex the stability of the amino-linkage was not attributable to hydrogen bonding since the closest approaches between the amino-nitrogen and either oxygen or fluorine atoms exceeded 3.0 Å (Table 5). A study of the interligand angles (cyclopentadienyl ring excluded) also failed to reveal any evidence of large distortions from the values obtained for comparable complexes,[38-40] as might be expected if hydrogen bonding were to occur. Similarly, the deviations from linearity at the carbonyl carbons are no more pronounced than for $[\{\mathrm{W}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{CO})_3\}_2]$.[41]

The covalent radius of tungsten has been estimated[42] to fall in the region 1.57—1.61 Å, although it has been stressed[43,44] that covalent radii can be affected by factors such as the oxidation state and stereochemistry around a metal. The W–N bond length (2.27 Å) in the present complex then corresponds to a covalent radius for nitrogen of 0.66—0.70 Å, which is of the correct order of magnitude.[44] Few comparable complexes are known, although the tungsten–hydrazone distance falls between those W–N bond lengths previously found for pyridine-like ligands (±2.21 Å)[42,45] and for a nitrile ligand (2.37 Å).[46] Other bonding parameters of the hydrazone ligand correspond well with previously reported values.[34] The amino-nitrogen of the hydrazone group is situated 0.63 Å above the plane of the carbonyl carbons, towards the metal atom, which is comparable to the position of the ethyl group in $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})\mathrm{Et(CO)_3}]$.[39]

The bonding of carbonyl groups to tungsten has been described in some detail.[35] A value of 1.95 Å is considered normal for a W–C bond length and 1.14 Å for C–O, although W–C bond lengths of 1.97—2.08 Å have been reported.[47-49] In the present complex the W–C bond lengths vary from 2.01 to 2.03 Å and C–O bonds from 1.13 to 1.14 Å. The W–C–O angles fall between 174 and 179°, with the largest angle being observed for the carbonyl *trans* to the hydrazone ligand.

The five carbon atoms of the cyclopentadienyl ring lie in a plane with mean deviation 0.002 Å. The perpendicular distance from the tungsten atom to this plane (1.98 Å) is similar to the 2.01 Å observed in $[\{\mathrm{W}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{CO})_3\}_2]$.[41] The C–C distances vary from 1.41 to 1.46(1) Å (mean 1.44 Å). A variation of this magnitude has previously been ascribed[35,50] to localisation of electron density within the ring. This phenomenon has also been used to explain variations in the W–C bond lengths which result in a 'tilting' of the ring.[38,51] In the present complex the W–C distances vary between 2.28 and 2.38(1) Å, and seem to indicate a slight ring tilt away from the hydrazone and towards the C(2) carbonyl ligand.

The mode of co-ordination of a hydrazone ligand to a metal has generally been accepted[13-15] as occurring preferentially through the imino-nitrogen atom, from a number of *X*-ray studies on four- and five-co-ordinate complexes.[13-15,52-55] This is despite the fact that the imino-nitrogen atoms are predicted to be less basic than amino-nitrogens.[33] It is pertinent to note that the majority of studies have involved complexes containing substituted hydrazones of the type $\mathrm{NHR'NCR_2}$ ($\mathrm{R'}$ = Me or Ph) and that co-ordination to a metal through a substituted amino-nitrogen atom is not sterically favoured.[56] This has been demonstrated by reactions of substituted hydrazines (*e.g.* $\mathrm{NH_2NMe_2}$) with metal complexes to give products in which the hydrazine ligand bonds exclusively through the unsubstituted nitrogen.[56] Recently, one of us has shown that for the unsubstituted acetone hydrazone ligand in the octahedral complex $[\mathrm{Ru(NH_2NCMe_2)_2\{P(OMe)_3\}_4][BPh_4]_2}$,[34] an amino-linkage is preferred. The results now obtained for $[\mathrm{W}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{CO})_3(\mathrm{NH_2NCMe_2})][\mathrm{PF_6}]$ seem to confirm that when imino- and amino-nitrogens compete for the co-ordination site an amino-linkage is favoured by: (*i*) a more sterically crowded octahedral or seven-co-ordinate metal environment; and (*ii*) the presence of an unsubstituted amino-nitrogen.

Conclusion.—The substitution reactions of $[\mathrm{M}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{CO})_3(\mathrm{N_2H_4})]\mathrm{Cl}$ (M = Mo or W) with tertiary phosphorus ligands have been shown to provide a reliable high-yield route to $[\mathrm{M}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{CO})_3\mathrm{L}]^+$ cations, thus encouraging a more detailed study of the chemistry of this class of complexes. Further work is in progress to determine the influence of the ligand L on the reduction reaction with $\mathrm{Na[BH_4]}$ which converts a carbonyl group into a methyl ligand in $[\mathrm{M}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{CO})_3(\mathrm{PPh_3})]^+$.

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