Transition Metal Complexes of the Dipyrromethylidene (Dipyrrol-2-ylmethylene) Ligand, $L_nM[=C(C_4H_4N)_2]$, from Reaction between Ruthenium- and Osmium-bound Dichlorocarbene and Pyrrole: Structures of $[RuCl_2\{=CCl(C_4H_4N)\}(CO)(PPh_3)_2]$ and $[RuCl\{=C(C_4H_3N)(C_4H_4N)\}(CO)(PPh_3)_2]$

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$[MCl_2(=CCl_2)(CO)L_2]$ (M = Ru or Os: L = PPh_3) with pyrrole forms sequentially $[MCl_2\{=CCl(C_4H_4N)\}(CO)L_2]$ and $[MCl\{=C(C_4H_3N)(C_4H_4N)\}(CO)L_2]$; the latter is protonated by HCl to the dipyrromethylidene complex $[MCl_2\{=C(C_4H_4N)_2\}(CO)L_2]$.

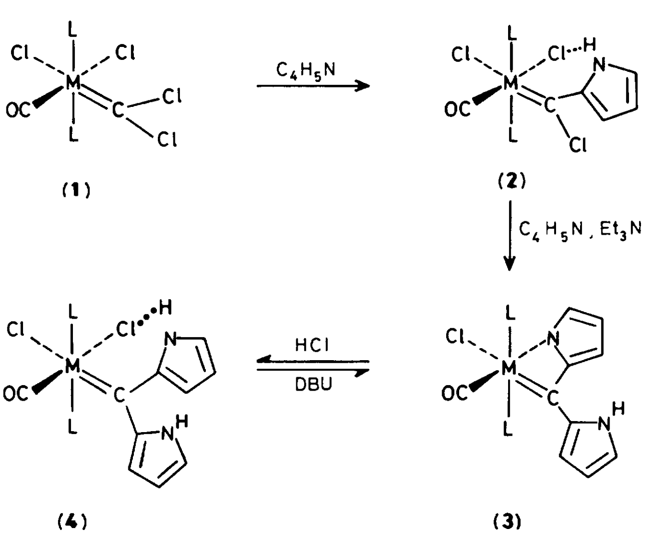
Metal-bound electrophilic dihalocarbene ligands can, in an intramolecular reaction, add to the phenyl rings of *cis*-co-ordinated triphenylphosphine ligands.[1] In a related intermolecular version of this reaction, the electrophilic carbene centre in $[MCl_2(=CCl_2)(CO)(PPh_3)_2]$ (M = Ru or Os)[2,3] has been found to add to the aromatic heterocycle pyrrole. Herein we report (i) the reaction with pyrrole which produces the first chloro-pyrrolylcarbene and dipyrromethylidene complexes, (ii) that the unprotected N–H in the C-bound pyrrolyl group in these complexes facilitates further chemical reaction and a reversible intramolecular N-metallation reaction occurs on exposure of the dipyrromethylidene complex to base, (iii) the structure of $[RuCl_2\{=CCl(C_4H_4N)\}(CO)(PPh_3)_2]$ which reveals an unusual hydrogen-bonding interaction, and (iv) the structure of $[RuCl\{=C(C_4H_3N)(C_4H_4N)\}(CO)(PPh_3)_2]$ with a chelate ligand involving both carbene and amido-donor functions.

The complex $[RuCl_2(=CCl_2)(CO)(PPh_3)_2]$ (**1a**) when heated with pyrrole (~20 equiv.) under reflux in benzene for 2 h forms the yellow, monochloro-pyrrolylcarbene complex

$[RuCl_2\{=CCl(C_4H_4N)\}(CO)(PPh_3)_2]$ (**2a**)† in high yield (Scheme 1). The pyrrolyl group in this complex has been shown to bond to C(carbene) *via* the carbon atom in the ring 2-position, not by the nitrogen atom. The i.r. spectrum shows ν(NH) at the low value of 3135 cm^{-1} and the corresponding N–*H* resonance in the ^1H n.m.r. spectrum appears markedly downfield at δ 12.76. The resonance of the pyrrolyl carbon atom bound to C(carbene) is evident in the ^{13}C n.m.r. spectrum at δ 155.97.‡

Single crystal *X*-ray structure determination of $[RuCl_2\{=CCl(C_4H_4N)\}(CO)(PPh_3)_2]$§ revealed the molecular geometry depicted in Figure 1. The bond lengths and angles associated with the chloro-pyrrolylcarbene ligand suggest there is some contribution to the bonding from the resonance structure (**II**). Thus the pyrrolyl ring, C(1) and Ru are all coplanar (within 0.02 Å) and the Ru–C(1)–C(2) angle of 139.2(1)° is considerably larger than the 120° expected for an sp^2 hybridized carbon atom. The Cl(3) atom lies 0.114(4) Å out of the Ru–C(1)–pyrrolyl plane and the C(1)–Cl(3) bond distance of 1.826(13) Å is very long and well outside the range of C–Cl distances (1.694—1.780 Å) reported for other dichloro- and monochloro-carbene complexes.[4,5] In addition, the carbon–carbon and carbon–nitrogen bond lengths alternate in the sense that the distances C(1)–C(2), C(3)–C(4), and C(5)–N are all shorter than the distances C(2)–C(3), C(4)–C(5), and C(2)–N.

The pyrrolyl ring is oriented so that the nitrogen atom is adjacent to the metal bound chloride, Cl(2). This conformation allows the formation of an intramolecular N–H·····Cl hydrogen bond between the pyrrole and Cl(2) with N·····Cl and N···H distances of 3.00(1) and 2.29 Å and associated N–H···Cl angle of 133.1°. This hydrogen-bonding is undoubtedly responsible for the observed low value of ν(N–H) in the i.r. spectrum and must persist in solution to explain the low-field resonance for the N–H proton in the ^1H n.m.r. spectrum.



a; M = Ru
b; M = Os

Scheme 1. Reaction of $MCl_2(=CCl_2)(CO)L_2$ with pyrrole. (M = Ru, Os; L = PPh_3; DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene)

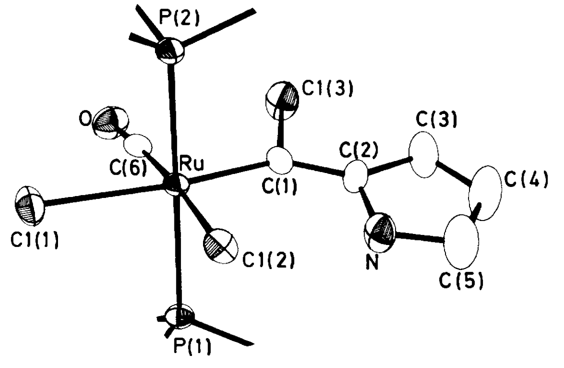
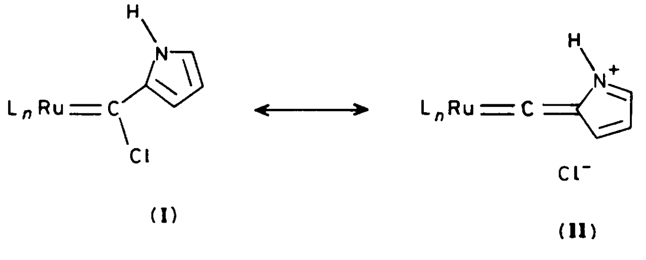


Figure 1. Molecular structure of $[RuCl_2\{=CCl(C_4H_4N)\}(CO)(PPh_3)_2]$ (**2a**) (phenyl rings omitted for clarity). Important bond lengths (Å) and angles (°): Ru–P(1) 2.437(3), Ru–P(2) 2.418(3), Ru–Cl(1) 2.512(3), Ru–Cl(2) 2.461(3), Ru–C(6) 1.857(16), Ru–C(1) 1.949(12), C(1)–Cl(3) 1.826(13), C(1)–C(2) 1.36(2); Ru–C(1)–Cl(3) 116.4(6), Ru–C(1)–C(2) 139.2(10), C(2)–C(1)–Cl(3) 104.4(9), C(1)–C(2)–N 120.2, Cl(2)–Ru–C(1) 94.6, C(1)–Ru–C(6) 91.1(6), C(6)–Ru–Cl(1) 81.2(4), Cl(1)–Ru–Cl(2) 93.2(1).



Compound (**2a**) provides the first example of a C-bound pyrrolylcarbene complex in which the pyrrolyl group bears no other substituents,[6,7] and is only the second structurally characterized monochlorocarbene complex to be reported.[5]

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† All new compounds have satisfactory elemental analyses. Selected spectral data are as follows: Important i.r. absorptions (cm^{-1}) measured as Nujol mulls between KBr plates: (**2a**) 1513, 1406, 1344, 1153, 1055, 877, 784 $\{=C[Cl]C_4H_4N\}$; (**3a**) 1558, 1510, 1470, 1320, 1248, 1120, 1025, 980, 879, 875, 830, 785 $\{=C[C_4H_3N]C_4H_4N\}$; (**4a**) 1515, 1345, 1275, 1149, 1057, 882, 815, 788 $\{=C[C_4H_4N]_2\}$. ^1H n.m.r. resonances of pyrrole protons (δ) and solvent used: (**2a**) (CD_2Cl_2) 12.74, s, 1H (N–H); 6.92, m, 1H; 6.47, m, 1H; 5.93, m, 1H. (**3b**) ($CDCl_3$) 7.84, s, 1H (N–H); 7.06, m, 1H; 6.59; m, 1H; 6.15, m, 2H; 5.94, m, 1H; 5.73, m, 1H. (**4a**) ($CDCl_3$) 13.46, s, 1H (N–H); 7.02, s, 1H(N–H); 6.97, m, 1H; 6.62, m, 1H; 6.13, m, 1H; 6.05, m, 1H; 5.85, m, 1H; 5.63, m, 1H. ^{13}C n.m.r. resonances of pyrrole carbon atoms (δ) and solvent used: (**2a**) (CD_2Cl_2) 155.97 (quat. carbon) 138.42, 122.56, 114.48. (**3b**) (CD_2Cl_2) 154.00 (quat. carbon), 140.99 (quat. carbon), 140.74, 118.54 (2 resonances coincident), 114.85, 114.63, 112.62. (**4a**) ($CDCl_3$) 154.44 (quat. carbon), 149.43 (quat. carbon), 135.66, 122.96, 121.78, 114.91, 113.40, 110.21.

‡ Signal(s) absent in the 135° DEPT editing sequence.

§ *Crystal data* for (**2a**): $C_{42}H_{34}Cl_3NOP_2Ru$, $M = 838.12$, monoclinic, $P2_1/n$, $a = 14.423(2)$, $b = 14.041(4)$, $c = 19.838(3)$ Å, $\beta = 92.76(1)°$, $U = 4011.4$ Å^3, $D_c = 1.39$ g cm^{-3} for $Z = 4$, $F(000) = 1872$, $\lambda(Mo\text{-}K_\alpha) = 0.71069$ Å, $\mu = 6.96$ cm^{-1}. 2802 observed data $[I > 3\sigma(I)]$ were collected at 292 K on a Nonius CAD-4 diffractometer. The structure was solved by Patterson and Fourier techniques and refined by full-matrix least squares to $R = 0.064$, $R_w = 0.069$.

Crystal data for (**3a**): $C_{44}H_{38}Cl_2N_2OP_2Ru$, $M = 844.72$, monoclinic, $P2_1/n$, $a = 14.765(2)$, $b = 18.188(1)$, $c = 15.265(2)$ Å, $\beta = 106.54(1)°$, $U = 3929.7$, $D_c = 1.43$ g cm^{-3} for $Z = 4$, $F(000) = 1728$, $\lambda(Mo\text{-}K_\alpha) = 0.71069$ Å, $\mu = 6.47$ cm^{-1}. 2881 observed data $[I > 3\sigma(I)]$ collected on a Nonius CAD-4 diffractometer at 290 K. The structure was solved as for (**2a**), $R = 0.057$, $R_w = 0.059$.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

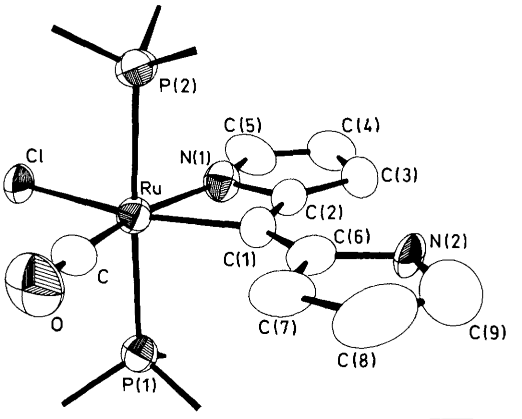

Figure 2. Molecular structure of [$RuCl\{=C(C_4H_3N)C_4H_4N\}(CO)(PPh_3)_2$] (**3a**) (phenyl rings omitted for clarity). Important bond lengths (Å) and angles (°): Ru–N(1) 2.172(9), Ru–C(1) 2.017(10), Ru–P(1) 2.402(3), Ru–P(2) 2.406(3) Ru–Cl 2.554(3), Ru–C 1.836(12), C(1)–C(2) 1.423(14), C(1)–C(6) 1.399(14); Cl–Ru–C 101.2(3), C–Ru–C(1) 99.7(5), C(1)–Ru–N 65.4(4), N(1)–Ru–Cl 93.6(2), Ru–N(1)–C(2) 90.9(6), N(1)–C(2)–C(1) 106.9(8), C(2)–C(1)–Ru 96.7(7), Ru–C(1)–C(6) 137.2(8).

Under more vigorous conditions the carbene chloride of (**2a**) is displaced by another pyrrolyl group (in what may be viewed as another electrophilic substitution reaction) and the complex [$RuCl\{=C(C_4H_3N)(C_4H_4N)\}(CO)(PPh_3)_2$] (**3a**) is formed (Scheme 1). A large excess of pyrrole (~90 equiv.), the presence of a base such as triethylamine, and heating under reflux in benzene for 3 h are required for complete reaction. Compound (**3a**) can be prepared directly from (**1a**) under similar conditions.

The stretching frequency of the carbonyl ligand in (**3a**) appears in the i.r. spectrum at 1906 cm^{-1} (CH_2Cl_2 solution). This is a significant drop from the ν(CO) value for complex (**2a**) and reflects the increased donor capabilities of the new amidocarbene chelate ligand in this complex. In the ^{13}C n.m.r. spectrum the pyrrolyl carbon atoms which are directly bound to C(carbene) resonate at δ 150.8 and 139.0.‡

Single crystal *X*-ray structure determination of the complex [$RuCl\{=C(C_4H_3N)(C_4H_4N)\}(CO)(PPh_3)_2$]§ revealed the geometry depicted in Figure 2. The two pyrrolyl rings, C(carbene), and the ruthenium atom are all coplanar. One of the rings is directly bound to ruthenium through the nitrogen atom, forming a four-membered strained metallacycle. The Ru–N bond is readily cleaved by hydrochloric acid and the dipyrromethylidene complex [$RuCl_2\{=C(C_4H_4N)_2\}(CO)(PPh_3)_2$] (**4a**) is formed in high yield (Scheme 1). This protonation reaction is reversible and addition of base to a solution of (**4a**) returns (**3a**) quantitatively. In crystalline samples of (**4a**) one of the ν(N–H) bands is at the very low frequency of 3041 cm^{-1}, suggesting that one of the pyrrole N–*H* atoms is hydrogen bonded, presumably to a *cis* chloride ligand as in (**2a**). The two pyrrole carbon atoms that are bound to C(carbene) resonate in the ^{13}C n.m.r. spectrum at δ 154.4 and 149.4.‡ The osmium dichlorocarbene complex (**1b**) also reacts with pyrrole and the osmium analogues (**2b**, **3b**, **4b**) of the new ruthenium complexes have been isolated (Scheme 1).

The new chloro-pyrrolylcarbene and dipyrromethylidene ligands in complexes (**2**)—(**4**) provide scope for much further chemical elaboration. In particular, the dipyrromethylidene ligand should function as a chelating N,N-donor ligand towards other metal centres, and this possibility is currently under study.

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