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Synthesis of 2-Pyrrolyl Complexes of Ruthenium and Osmium via Hydrolysis of a Chloro(pyrrolyl)carbene Ligand or via Transmetalation Reactions Using (2-Pyrrolyl)mercuric Chloride

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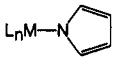
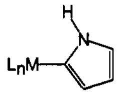
Summary: The chloro(2-pyrrolyl)carbene complex Ru(=C[Cl]-2-$C_4H_3NH)Cl_2(CO)(PPh_3)_2$ (1) undergoes hydrolysis and rearrangement to give the σ-bound 2-pyrrolyl complex Ru(2-$C_4H_3NH)Cl(CO)_2(PPh_3)_2$ (2). Compound 2, and the osmium analogue Os(2-$C_4H_3NH)Cl(CO)_2(PPh_3)_2$ (4), can be prepared by reaction of (2-pyrrolyl)mercuric chloride (3) with the low-oxidation-state compounds $M(CO)_2(PPh_3)_3$ (M = Ru, Os), respectively. Key steps in the synthesis of compound 3 involve protection of the pyrrolic nitrogen atom with a lithiocarboxylate function followed by selective lithiation and then mercuration in the ring 2-position.

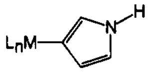
The two main coordination modes that have been reported for the pyrrolyl anion can be represented by the generalized structures I and IV.[1] Until our initial report[2] and a more recent report by Gladysz et al.,[3] 2-metallopyrroles (II) were unknown, and we are unaware of examples of simple 3-metallopyrroles (III).



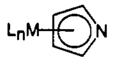
I



II



III



IV

We have previously reported that the chloro(pyrrolyl)carbene complex Ru(=C[Cl]-2-$C_4H_3NH)Cl_2(CO)(PPh_3)_2$ (1) can be easily prepared from the reaction of Ru(=$CCl_2)Cl_2(CO)(PPh_3)_2$ with pyrrole.[4] We now report that hydrolysis of compound 1 gives, after reverse migration, a 2-pyrrolyl complex of ruthenium. In an attempt to develop an alternative and more general route to C-metalated derivatives of unprotected pyrrole, we have prepared the hitherto unknown compound (2-pyrrolyl)mercuric chloride and established that this can be used as a 2-pyrrolyl transfer reagent to suitable derivatives of the transition metals ruthenium and osmium.

Treatment of dichloromethane, benzene, or tetrahydrofuran solutions of Ru(=C[Cl]-2-$C_4H_3NH)Cl_2(CO)(PPh_3)_2$ (1) with water or aqueous solutions of the bases sodium hydroxide and sodium carbonate results in the rapid formation of the 2-pyrrolyl dicarbonyl complex Ru(2-$C_4H_3NH)Cl(CO)_2(PPh_3)_2$ (2). Samples prepared in this way are often contaminated with small amounts of $RuCl_2(CO)_2(PPh_3)_2$. A superior synthesis involves passage of a dichloromethane solution of 1 down a silica gel column using dichloromethane as eluent. Pure 2 is obtained from the eluent in 72% yield.[5]

The mechanism proposed for the formation of 2 is depicted in Scheme 1. Hydrolysis of the reactive carbon–chlorine bond followed by loss of HCl and reverse migration of the pyrrolylacyl intermediate leads directly to 2.[6]

[•] Abstract published in *Advance ACS Abstracts,* June 1, 1994.

[1] A number of complexes with structures I and IV (or distorted versions of these idealized structures) have been reported. For lead references see: (a) Bynum, R. V.; Zhang, H.-M.; Hunter, W. E.; Atwood, J. L. *Can. J. Chem.* **1986,** *64,* 1304. (b) Kershner, D. L.; Basolo, F. *J. Am. Chem. Soc.* **1987,** *109,* 7396. In addition, coordination of the pyrrolyl anion to metal clusters is known; e.g.: Day, M. W.; Hardcastle, K. I.; Deeming, A. J.; Arce, A. J.; De Sanctis, Y. *Organometallics* **1990,** *9,* 6. The coordination of free pyrrole to pentaammineosmium(II) has also been reported: Cordone, R.; Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1989,** *111,* 5969.

[2] Clark, G. R.; Ng, M. M. P.; Rickard, C. E. F.; Roper, W. R.; Snowball, R. E.; Wright, L. J. *Abstracts of Papers,* International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, 1989; American Chemical Society: Washington, DC, 1989; INOR 725.

[3] Johnson, T. J.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1993,** *12,* 4728.

[4] Clark, G. R.; Hodgson, D. J.; Ng, M. M. P.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J. *J. Chem. Soc., Chem. Commun.* **1988,** 1552.

[5] Compound 2 was prepared in the following ways. (a) Ru(=C[Cl]-2-$C_4H_3NH)Cl_2(CO)(PPh_3)_2$ (0.200 g) was dissolved in dichloromethane (20 mL) and the orange solution passed through a silica gel column (8 cm × 3 cm) using dichloromethane as eluent. A pale yellow-green band was collected and the solvent volume reduced to ca. 25 mL under reduced pressure. Ethanol was added and the solution further reduced in volume to effect crystallization of greenish cream microcrystals of 2. Recrystallization from dichloromethane/ethanol gave pure 2 as greenish cream crystals (0.134 g, 72%). (b) $Ru(CO)_2(PPh_3)_3$ (0.200 g) and (2-pyrrolyl)mercuric chloride (0.070 g, 1.1 equiv) were heated under reflux in deoxygenated benzene (20 mL) for 20 min. The yellow suspensions turned cloudy orange within seconds, the color intensified within minutes to a murky reddish brown suspension, and the precipitation of elemental mercury was observed. The flask was cooled to room temperature, and the solvents were removed under vacuum. The resulting product was redissolved in dichloromethane and filtered through Celite. Ethanol was added and the solvent evaporated under reduced pressure until the pale greenish cream product had crystallized from solution. The product was recrystallized from dichloromethane/ethanol to give pure 2 (0.098 g, 56%). Data for Ru(2-$C_4H_3NH)Cl(CO)_2(PPh_3)_2$ (2): IR (Nujol mull, cm^{-1}) 2032, 1971 ν(CO), 3402, 1512, 1413, 1064, 1030 (pyrrolyl bands), 302 ν(RuCl); ^1H NMR ($CDCl_3$, δ in ppm, TMS at δ 0) 8.70 (s, 1H, N*H*), 7.23–7.39 (m, 30H, Ph *H*), 6.49 (m, 1H, py C*H*), 6.06 (m, 1H, py C*H*), 5.64 (m, 1H, py C*H*), 5.29 (s, 1H, 0.5CH_2Cl$_2$ of crystallization); ^{13}C NMR ($CDCl_3$, δ in ppm, TMS at δ 0, *J* in Hz) 215.15 (apparent singlet, CO), 194.63 (apparent singlet, *C*O), 134.31 (t, *J*(CP) 5.2, *C*(o/m)), 131.32 (t, *J*(CP) 23, *C*(ipso)), 129.95 (s, *C*(para)), 127.85 (t, *J*(CP) 5.2, *C*(o/m)), 119.33 (s, py *C*H) 118.44 (s, py *C*H), 108.59 (s, py *C*H) (quaternary py C resonance not observed); ^{31}P NMR ($CDCl_3$, δ in ppm, H_3PO_4 at δ 0) 21.30 (s, *P*Ph$_3$). Anal. Calcd for $C_{42}H_{34}ClNO_2P_2Ru \cdot 0.5CH_2Cl_2$: C, 62.71; H, 4.72; N, 1.75. Found: C, 62.55; H, 4.27; N, 1.75.

[6] In a related reaction the chloro(phenyl)carbene complex $OsCl_2$(=C[Cl]Ph)(CO)$(PPh_3)_2$ undergoes hydrolysis and rearrangement to give a σ-aryl dicarbonyl complex: Clark, G. R.; Cochrane, C. M.; Marsden, K.; Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **1996,** *315,* 211. The (2-pyrrolyl)rhenium compound reported in ref 3 was prepared via direct reaction of pyrrole with a rhenium triflate derivative followed by deprotonation of the resulting carbon-ligated N-protonated iminoacyl intermediate, or via acid-catalyzed rearrangement of a coordinated N-pyrrolyl derivative. Both these routes and that involving the hydrolysis/rearrangement of a chloro(pyrrolyl)carbene ligand described in this paper will probably not prove to be general routes to transition-metal 2-pyrrolyl complexes.

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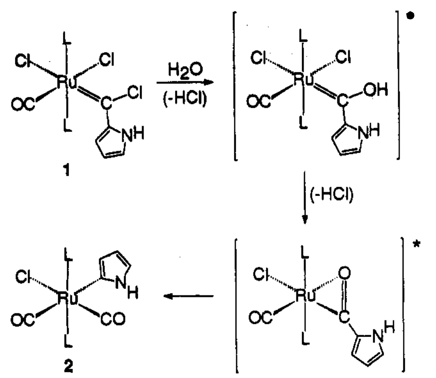
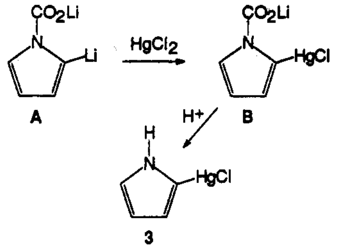
Scheme 1[a]



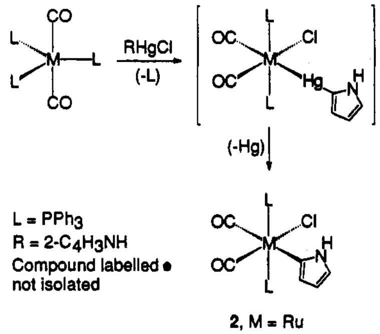
[a] L = PPh_3. Compounds labeled with an asterisk were not isolated.

Scheme 2



3

Scheme 3[a]



2, M = Ru
4, M = Os

[a] L = PPh_3 and R = $2\text{-}C_4H_3NH$. The compound labeled with an asterisk was not isolated.

The formulation of **2** as a 2-pyrrolyl dicarbonyl derivative is fully supported by IR and NMR spectral data.[5] Two ν(CO) bands are observed in the IR spectrum, indicating two mutually cis carbonyl ligands. A sharp band at 3402 cm^{-1} is assigned to ν(NH), and a weak band at 302 cm^{-1} is assigned to ν(RuCl). In the ^1H NMR spectrum a broad resonance at 8.70 ppm, which is integrated for one proton vs the PPh_3 protons (30), is assigned to NH. The three CH pyrrolyl resonances are observed at 5.64 (m), 6.06 (m), and 6.49 (m) ppm. It would be expected that the position of substitution at pyrrole would be retained during this reverse migratory insertion reaction and that the product would be therefore be the (2-pyrrolyl)ruthenium derivative. This is confirmed by the fact that the same compound **2** is also formed by oxidative addition of (2-pyrrolyl)mercuric chloride to $Ru(CO)_2(PPh_3)_3$ (vide infra).

In view of the novel character of this compound, a simple and more general method of synthesis was sought. As there are good precedents for the transfer of σ-aryl groups from mercury to ruthenium and osmium,[7] a route involving σ-pyrrolyl group transfer from (2-pyrrolyl)mercuric chloride (**3**) was considered. Although direct mercuration of the heterocycles thiophene and furan proceeds smoothly under the appropriate conditions to give the corresponding monomercurated derivatives, direct mercuration of pyrrole results in the formation of polymercurated products.[8] An alternative approach involving the reaction of (pyrrolyl)-magnesium bromide with mercuric chloride gives oligomeric pyrrole products, rather than **3**.

The required (2-pyrrolyl)mercuric chloride can be synthesized using a procedure developed by Katritzky and Akutagawa for the selective functionalization of pyrrole in the 2-position.[9] The key feature of this approach involves initial protection of the pyrrolic nitrogen atom with a lithiocarboxylate function. Subsequent C-lithiation is then directed selectively to the 2-position. It was found that reaction of the C-lithiated intermediate A (Scheme 2) with mercuric chloride, followed by carefully controlled acidolysis and decarboxylation, gives **3** in ca. 20% overall isolated yield.[10]

(2-Pyrrolyl)mercuric chloride (**3**) is a white crystalline solid. A strong band in the IR spectrum at 3358 cm^{-1} is assigned to ν(NH), and a band at 333 cm^{-1} is assigned to ν(HgCl). The NH resonance in the ^1H NMR spectrum appears as a broad signal centered at 8.46 ppm, and the three CH resonances are observed at 7.09 (m), 6.47 (dd), and 6.32 (m). The structure of **3** has been determined by a single-crystal X-ray structure determination.[10]

The 2-pyrrolyl group of compound **3** can be easily transferred to suitable transition-metal substrates. Thus, treatment of solutions of $M(CO)_2(PPh_3)_3$ (M = Ru, Os) with **3** gives the corresponding 2-pyrrolyl derivatives $Ru(2\text{-}C_4H_3NH)Cl(CO)_2(PPh_3)_2$ (**2**; 56%)[5] and $Os(2\text{-}C_4H_3NH)Cl(CO)_2(PPh_3)_2$ (**4**; 58%).[11] The reactions also involve the formation of elemental mercury and probably proceed via oxidative addition of the mercury–chloride bond to the transition-metal center, followed by loss of elemental mercury and formation of the metal–carbon bond (Scheme

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(7) Rickard, C. E. F.; Roper, W. R.; Taylor, G. E.; Waters, J. M.; Wright, L. J. *J. Organomet. Chem.* **1990**, *389*, 375.

(8) Katritzky, A. R. *Handbook of Heterocyclic Chemistry*; Pergamon Press: Oxford, U.K., 1985.

(9) Katritzky, A. R.; Akutagawa, K. *Org. Prep. Proced. Int.* 1988, *20*, 585.

(10) $(2\text{-}C_4H_3NH)HgCl$ (**3**) was prepared in the following way: lithium 2-lithiopyrrole-*N*-carboxylate was generated in situ as described in ref 9 (starting with 2.0 mL of pyrrole). A solution of mercuric chloride (7.5 g, 1 equiv) in THF (15 mL) was added at −78 °C. After 2 h the solution was warmed to 20 °C and the resulting mixture acidified with dilute sulfuric acid to remove the carboxylate protecting group from nitrogen. After neutralization, the solution was extracted with dichloromethane. Removal of the solvent under reduced pressure and recrystallization from dichloromethane/hexane/ethanol afforded pure **3** in ca. 20% yield. Full experimental details for the synthesis of **3** and the results of a single-crystal X-ray structure determination of this compound will be published separately. Data for $(2\text{-}C_4H_3NH)HgCl$ (**3**): IR (Nujol mull, cm^{-1}) 3358 ν(NH), 3100, 1526, 1408, 1346, 1242, 1171, 1107, 1074, 1028, 910, 878, 793, 722, 554 (pyrrolyl bands), 333 ν(HgCl); ^1H NMR ($CDCl_3$, δ in ppm, TMS at δ 0, J in Hz) 8.46 (s, 1H, N*H*), 7.09 (m, 1H, C*H*), 6.47 (dd, 1H, C*H*, J(HH) 5.6, 2.8), 6.32 (m, 1H, C*H*), 5.29 (s, 0.5H, $0.25CH_2Cl_2$ of crystallization); ^{13}C NMR (DMSO-d_6, δ in ppm, DMSO-d_6 at δ 39.43) 107.21 (s, *C*H), 115.55 (s, *C*H), 119.51 (s, *C*H), (quaternary C resonance not observed). Anal. Calcd for $C_4H_4ClHgN\cdot 0.25CH_2Cl_2$: C, 15.79; H, 1.40; N, 4.33. Found: C, 15.33; H, 1.65; N, 4.63.

(11) Data for $Os(2\text{-}C_4H_3NH)Cl(CO)_2(PPh_3)_2$ (**4**): IR (Nujol mull, cm^{-1}) 3411 ν(NH), 2022, 1971 ν(CO), 1517, 1418, 1224, 1073 (pyrrolyl bands); ^1H NMR ($CDCl_3$, δ in ppm, TMS at δ 0, J in Hz) 7.97 (s, 1H, N*H*), 7.23–7.37 (m, 30H, P*Ph*$_3$), 6.43 (m, 1H, py C*H*), 6.04 (dd, 1H, py C*H*, J(HH) 5.30, 2.51), 5.66 (m, 1H, py C*H*); ^{13}C NMR ($CDCl_3$, δ in ppm, TMS at δ 0, J in Hz) 134.36 (t, *C*(o/m), J(CP) 5.2), 131.04 (t, *C*(ipso), J(CP) 26.0), 130.06 (s, *C*(para)), 127.81 (t, *C*(o/m), J(CP) 5.1), 119.92 (s, py *C*H), 118.96 (s, py *C*H), 108.88 (s, py *C*H), (quaternary py C and CO resonances not observed); ^{31}P NMR ($CDCl_3$, δ in ppm, H_3PO_4 at δ 0) −9.9 (s, *P*Ph$_3$). Anal. Calcd for $C_{42}H_{34}ClNO_2P_2Os$: C, 57.83; H, 3.93; N, 1.69. Found: C, 57.89; H, 3.86; N, 1.63. Details of the experimental procedure for the synthesis of **4** are given in the supplementary material.

3).[12] The very close similarity of the ^{1}H and ^{13}C NMR resonances of the pyrrolyl groups in **2** and **4** strongly suggests that substitution in the 2-position is retained in **4** also.

The reaction involving oxidative addition of (2-pyrrolyl)-mercuric chloride (**3**) to $Ru(CO)_2(PPh_3)_3$ provides a more convenient, alternative route to **2**. It is anticipated that a wide range of different 2-pyrrolyl transition-metal derivatives will become accessible through reaction of **3** with suitable transition-metal substrates.

The 2-metallopyrrole compounds that are described in this paper are among the first examples of this new class of compound to be reported. The coordinated 2-pyrrolyl ligand promises to display an interesting and varied chemistry, and examples of electrophilic addition to C-5 and of migratory insertion involving the metal–carbon bond will be reported in a forthcoming paper.

Acknowledgment. We thank the University of Auckland Research Committee for partial support of this work through grants in aid, the New Zealand Universities Grants Committee for the award of a postgraduate scholarship to M.M.P.N., and Dr. C.E.L. Headford for experimental assistance.

Supplementary Material Available: Textual description of experimental details for the synthesis of compound **4** (1 page). Ordering information is given on any current masthead page.

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[12] Oxidative addition of arylmercury halides to Pt(0) proceeds through an intermediate which is analogous to that proposed in Scheme 3: Sokolov, V. I.; Reutov, O. A. *Coord. Chem. Rev.* **1978**, *27*, 89.