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RHODIUM(I) AND IRIDIUM(I) BIS(PYRAZOLYL)BORATES

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Summary

The complexes $(CO)_2M(H_2BPz_2)$ and $(CO)(Ph_3P)M(H_2BPz_2)$ [M = Rh, Ir; Pz = 1-pyrazolyl, 3,5-dimethyl-1-pyrazolyl] were prepared. Their properties are discussed and compared with those of the corresponding β-diketonates.

Introduction

Poly(pyrazolyl)borate ligands, $[Pz_nBH_{4-n}]^-$ (Pz = pyrazolyl) extensively investigated by Trofimenko [1], are useful for obtaining volatile metal complexes, suitable for mass spectral and ESCA studies, in line with investigations already begun by our group on organometallic β-diketonates [2].

Therefore certain suitable new bis(pyrazolyl)borates of dicarbonylrhodium(I) and dicarbonyliridium(I) were prepared and are described here. Physicochemical data will be published elsewhere.

Other researchers [3-5] have investigated reactions of poly(pyrazolyl)borates with certain rhodium or iridium compounds. Under their experimental conditions boron-free products or insoluble, polynuclear species were obtained in certain cases, e.g. $[(CO)_2RhPz]_2$, $[Rh_2(HBPz_3)_2(CO)_3]_n$ or $[Rh_2(BPz_4)_2]_n$. In other cases no complex could be isolated, e.g. with iridium carbonyl halides or with the bis(3,5-dimethyl-1-pyrazolyl)borate ligand.

Experimental

Evaporation was always carried out under reduced pressure. NMR spectra were recorded at 60 MHz in $CDCl_3$ solution. Mass spectra, recorded in the Bologna laboratory of Professor S. Pignataro, will be published elsewhere. Potassium bis(pyrazolyl)borate and bis(3,5-dimethyl-1-pyrazolyl)borate, prepared according to the method of Trofimenko [6], were crystallized from anisole and from toluene respectively.

cis-[Bis(1-pyrazolyl)dihydroborate]dicarbonylrhodium(I) (I)

Tetracarbonyldi-μ-chlorodirhodium(I) (600 mg, 1.50 mmol) were added to a stirred suspension of potassium bis(1-pyrazolyl)dihydroborate (700 mg, 3.76 mmol) in petroleum ether (30 ml). After 20 min the suspension was filtered and the yellow solution was evaporated to dryness, yielding a dirty-yellow solid (648 mg). The compound was purified by sublimation at 35-50°/0.1 Torr, yielding a yellow analytical sample, m.p. 66° (the colour changes to red on melting). (Found: C, 31.46; H, 2.54; N, 18.51. $C_8H_8BN_4O_2Rh$ calcd.: C, 31.4; H, 2.61; N, 18.3%.) NMR spectrum: τ 3.80 triplet (4H), and 2.40 ppm doublet (3H and 5H), $J \approx 2.2$ Hz. IR spectrum: (Nujol mull) 3080 w, 2430 m, 2390 m, 2330 (sh), 2295 (sh), 2280 m, 2084 s, 2020 s, 1510 m, 1468 s, 1408 s, 1376 m, 1302 s, 1260 w, 1210 m, 1202 m, 1194 m, 1176 w, 1168 s, 1154 s, 1102 w, 1090 w, 1067 s, 1033 (br, sh), 991 w, 924 w, 900 w, 883 s, 860 w, 805 w (br), 770 (sh), 765 (sh), 758 s, 731 w, 720 m, 632 m, 620 m, 612 (sh), 516 m, 498 w, 448 w, 330 w cm^{-1}; in cyclohexane 2420 m, 2390 (sh), 2245 (sh), 2220 (sh), 2082 s, 2065 vw, 2013 s, 1985 vw cm^{-1}. The B—H vibrations are not well resolved. Electronic spectrum: (cyclohexane) 353 (ϵ 3160) 261 nm (10, 100). Mass spectrum: the parent ion could not be detected, the highest ion being found at *m/e* 305, i.e. ($P - 1$).

cis-[Bis(1-pyrazolyl)dihydroborate]dicarbonyliridium(I) (II)

Iridium powder was mixed with the same weight of sodium chloride and the mixture was heated at ca. 600° in a stream of chlorine. The resulting crude sodium hexachloroiridate(IV) was heated at 120° under 200 atm of carbon monoxide for 20 h in a test-tube surrounded externally by a coil of clean copper wire. A second, smaller, coil was inserted inside the test-tube in the free space above the solid. After the reaction was complete the coils were covered with a white crystalline material, probably CuCl.

The tobacco-coloured mixture, ca. 0.5 g, which is known [7] to contain "$Na[Ir_2(CO)_3Cl_{3.8}]$", was suspended in petroleum ether (40 ml). Potassium bis(pyrazolyl)dihydroborate (200 mg) were suspended in the same solvent (40 ml). These suspensions upon mixing turned yellow. After stirring for 20 min, the filtered solution was evaporated to dryness and the orange residue was sublimed at ca. 50-60°/0.1 Torr, to yield an orange analytical sample, m.p. 96° (yield 400 mg). (Found: C, 24.76; H, 2.00; N, 14.42. $C_8H_8BIrN_4O_2$ calcd.: C, 24.3; H, 2.02; N, 14.2%.) NMR spectrum: τ 3.73 triplet (4H) 2.43 doublet and 2.31 ppm doublet (3H and 5H), J 2.2 Hz. IR spectrum: (Nujol mull) 3120 w, 3100 w, 2440 m, 2370 m, 2280 m, 2070 s, 2005 s, 1981 m (sh), 1515 m, 1468 s, 1418 s, 1382 s, 1318 s, 1228 s, 1209 m, 1200 m, 1172 s, 1158 s, 1115 w, 1072 s, 892 w, 885 s, 860 vw, 852 w, 777 m, 762 s, 720 m, 636 s, 620 m, 614 m, 543 m, 533 m, 510 w, 338 w cm^{-1}; in petroleum ether 2430 w, 2400 (sh), 2080 s, 2058 w, 2010 s, 1975 vw cm^{-1}. Mass spectrum: the parent ion could not be found, the highest ion being detected at *m/e* 395, i.e. (P—1). Electronic spectrum (cyclohexane): 408 (ϵ 720), 368 (3,650), 321 (3,260), 273 nm (16,000).

$(Ph_3P)(CO)Rh[Pz_2BH_2]$ (III)

To a solution of compound I (91 mg) in petroleum ether was added triphenylphosphine (30 ml/160 mg) in the same solvent. The precipitate which formed immediately was filtered and washed with the same solvent, yielding a canary-yellow analytical sample, m.p. 125-126°. (Found: C, 54.92; H, 4.14; N, 10.10. $C_{25}H_{23}BN_4OPRh$ calcd.: C, 55.6; H, 4.27; N, 10.4%.) Infrared spectrum: (Nujol mull) 2425 m, 2368 m, 2296 w, 2289 m, 1969 vs, 1920 w cm^{-1}. NMR spectrum: 4.34 (4H), triplet, 3.81 and 3.69 (3 and 5H), all three signals with unresolved fine structure, 3.0-2.1 ppm complex (aromatic).

$(Ph_3P)(CO)Ir[Pz_2BH_2]$ (IV)

The iridium compound II (40 mg) was dissolved in petroleum ether (20 ml) and triphenylphosphine (40 mg), in minimum amount of the same solvent, was added. The precipitate, which formed after 5 min, was filtered after 20 min, yielding a canary-yellow analytical sample, m.p. 155-156° (reddening). (Found C, 47.13; H, 3.46; N, 8.86. $C_{25}H_{23}BIrN_4OP$ calcd.: C, 47.7; H, 3.66; N, 8.9%.)

IR spectrum (Nujol mull); 2425 m, 2370 m (br), 2295 w, 2280 m, 1960 vs, 1910 w cm^{-1}. NMR spectrum: ca. 4.3 triplet (4H), ca. 3.75 and 3.5, multiplet with unresolved fine structure (3 and 5H), 2.8-2.1 ppm multiplet (aromatic).

cis-[Bis(3,5-dimethylpyrazolyl)dihydroborate] dicarbonylrhodium(I) (V)

Tetracarbonyl-μ-dichlorodirhodium(I) (0.40 g) in diethyl ether (30 ml) was added to a stirred suspension of potassium bis[1-(3,5-dimethylpyrazolyl)]-dihydroborate (0.50 g) in the same solvent (30 ml). A dark brown precipitate formed immediately. After 10 min the yellow, filtered solution was evaporated to dryness and the residue was extracted with petroleum ether. The extract was evaporated to dryness and the rather unstable residue was sublimed at once at 90-100°/ca. 0.05 Torr, to give an analytical sample (0.20 g, dec. above ca. 135°). (Found: C, 39.62; H, 4.44; N, 15.43. $C_{10}H_{16}BN_4O_2Rh$ calcd.: C, 39.85; H, 4.42; N, 15.45%.) NMR spectrum: 7.74 (s), 7.67 (s, Me) and 4.24 (s, 4H) ppm. IR spectrum: (Nujol mull) 2460 s, 2360 m, 2320 m, 2268 m, 2220 m, 2085 s, 2018 vs, 1971 m; (petroleum ether) 2081 s, 2075 w (sh), 2015 s cm^{-1}. Electronic spectrum (cyclohexane): 364 (ϵ 2,200), 287 nm (11,650).

Bis-[(3,5-dimethyl-1-pyrazolyl)dihydroborate] zinc(II) (VI)

This compound was obtained in 40% yield from equal quantities of zinc bromide and of the ligand in aqueous suspension. It was purified by recrystallization from $Et_2O/CHCl_3$ as needles, m.p. 235°. (Found: C, 50.93; H, 6.85; N, 23.67. $C_{20}H_{32}B_2N_8Zn$ calcd.: C, 51.0; H, 6.80; N, 23.80%.) NMR spectrum: 8.23 (s), and 7.65 (s, Me), 4.25 (s, 4H) ppm.

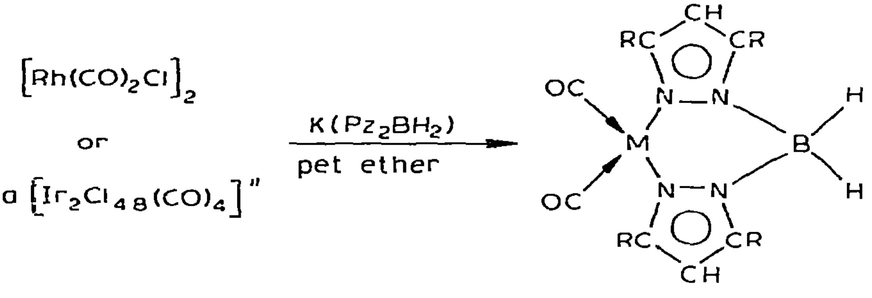
Bis-[(3,5-dimethyl-1-pyrazolyl)dihydroborate] copper(II) (VII)

This compound was obtained in 50% yield from an aqueous solution (30 ml) of $CuSO_4 \cdot 5H_2O$ (0.5 g) upon addition, with stirring, of the solid ligand (0.5 g) and was purified by recrystallization from CH_2Cl_2/Et_2O. The product was isolated as brown-violet crystals which became blue at ca. 201, green at ca. 260 and brown-violet at 268°. (Found: C, 51.24; H, 6.85; N, 23.71. $C_{20}H_{32}B_2CuN_8$ calcd.: C, 51.10; H, 6.82; N, 23.85%.)

The analogous cobalt(II) and nickel(II) compounds were prepared according to published methods [1, 6].

Results and discussion

The dicarbonyl derivatives were obtained readily according reaction 1.



(I : M = Rh, R = H;
II : M = Ir, R = H;
V : M = Rh, R = CH_3)

The compounds are air-stable and very soluble in organic solvents. They may be sublimed under reduced pressure.

The reactivity of $(CO)_2M(Pz_2BH_2)$ compounds I and II, is similar to that [8, 9] of the corresponding β-diketonates. A π-accepting ligand, such as Ph_3P, displaced one carbonyl group, giving yellow, air-stable compounds (eqn. 2). Under the same conditions, triethylamine and pyridine do not react.

$$(CO)_2M(Pz_2BH_2) + Ph_3P = CO + (CO)(Ph_3P)M(Pz_2BH_2) \qquad (2)$$

(III: M = Rh; IV: M = Ir)

Compounds I, II and V are yellow or orange-yellow in both the solid state and solution, whereas the analogous β-diketonates are red, green or dichroic in the solid state as a consequence of a metal—metal interaction [10] and are yellow in solution. The lack of such an interaction in the pyrazolylborates reported here is probably due to the non-planar conformation typical [11, 12] of the MNNBNN ring, while the planar β-diketonate ligand allows intermolecular contact between metal atoms in a square-planar coordination. In the mass spectra [14] of I and II no molecular ion (P^+), but only $(P-1)^+$ was observed and correspondingly, the highest ion observed in the mass spectra of nickel(II), zinc(II) and copper(II) bis(1-pyrazolyl)borate was $(P-1)^+$.

If the usual [12] pseudo-boat conformation of the MNNBNN ring is assumed, inspection of the molecular model shows that one of the B—H bonds points towards the metal, from which it is not too distant, although well beyond any bonding distance in the ground state. In the excited state, e.g. upon ionization in the mass spectrometer, the molecular ion loses one hydrogen atom per molecule of bis(pyrazolyl)borate rather easily, perhaps through a metal—hydrogen interaction of the type established in the ground state by Cotton [13] for one hydrogen atom of a BH_2 group in (trihaptocycloheptatrienyl)dicarbonylmolybdenum dihydrobis(3,5-dimethyl-1-pyrazolyl)borate. This hypothesis may account for the mass spectral properties, which differ from those of the corresponding β-diketonates, for which the parent ion was always detected [2].

The NMR spectra ($CDCl_3$) show all the signals required by the pyrazolyl group and the aromatic protons of III and IV, while the B—H hydrogens, quite evident in the infrared spectrum, could not be detected owing to coupling with ^{10}B and ^{11}B nuclei. The pyrazolyl protons give three signals, a triplet (4H) and two doublets (3 and 5H), in compound II, while in compound I the two doublets overlap in $CDCl_3$. An upfield shift (ca. 0.6-1.0 ppm) was observed in the heteroaromatic protons of compounds III and IV owing to the long range shielding of the phenyl groups; in addition, the two pyrazolyl rings are no longer equivalent.

Magnetic inequivalence is more evident in the Zn^{II} or $(CO)_2Rh^I$ derivatives of the bis(3,5-dimethyl-1-pyrazolyl)borate group; no other complex was investigated, cobalt and copper (II) derivatives being paramagnetic and nickel(II) sparingly soluble. In the $(CO)_2Rh$ derivative the two Me signals are less than 0.1 ppm apart, while in the zinc derivative they are separated by 0.57 ppm. The difference may be due to the diamagnetic shielding caused by the aromatic ring currents in the pyrazole group of the other $Pz_2BH_2^-$ moiety in the tetrahedrally coordinated zinc complex. This difference permits assignment of the higher field signal to the four methyl groups nearer the metal atom.

The infrared spectra of compounds I-V contain all the bands required by the pyrazolylborate, carbonyl, and triphenylphosphine ligands. Comparison of the spectra in the B—H stretching region and at ca. 1060 cm^{-1} (single band), between the square-planar nickel(II), copper(II) and the tetrahedral zinc(II) and cobalt(II) derivatives showed that in compounds I-V the ligand surround the metal is in a planar arrangement.

Carbonyl stretching absorptions are rather sensitive to the electron-withdrawing or -releasing ability of the groups bonded to the metal. Here they were found at values similar to those reported for the related acetylacetonates, suggesting that the net electronic effect of the two groups on the $\nu(CO)$ is quite similar.

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