Structure, electrochemistry and hydroformylation catalytic activity of the bis(pyrazolylborato)rhodium(I) complexes [RhBp(CO)P] [P=$P(NC_4H_4)_3$, PPh_3, PCy_3, $P(C_6H_4OMe\text{-}4)_3$].

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Rhodium complexes of formula [RhBp(CO)P] [Bp = bis(pyr-azolylborate), P = P(NC4H4)31, PPh32, PCy33,P(C6H4OMe-4)34] have been prepared by exchange of the acetylaceton-ate (acac−) ligand in [Rh(acac)(CO)P] complexes. The spec-troscopic and electrochemical properties as well as X-raydata of [Rh(acac)(CO)P] and [RhBp(CO)P] complexes havebeen compared with the aim to estimate the relative donorproperties of both anionic ligands (acac−and Bp−). The cyclicvoltammetric results indicate that the Bp−ligand behaves asa much stronger electron donor than acac−and a value of theLeverELligand parameter identical to that of the pyrazolateligand (−0.24 V vs. NHE for each coordinating arm) is pro-posed for the bis- and tris(pyrazolyl)borate ligands, whereasP(C6H4OMe-4)3is also shown to have an identicalELvalue(0.69 V) to that of P(NC4H4)3. An improved linear relationship between the oxidation potential and the sum of the ligandELvalues for square-planar RhIcomplexes is also obtained andadjusted values for the LeverSMandIMparameters for theRhI/RhIIredox couple are given. Thetransinfluence of phos-phanes was not observed in crystals of complexes2and3,incontrast to analogous acetylacetonato complexes in whichthe Rh−O bonds differ by ca. 0.04−0.06 A°. Complexes1−4arevery attractive precursors for hydroformylation catalysts andyields of aldehydes of 80−87% have been obtained with allcomplexes without extra phosphane as co-catalyst. Duringthe hydroformylation reaction, however, small amounts of acatalytically inactive [RhBp(CO)2] complex were formed.

Słowa kluczowe

Rhodium, N ligands, Electrochemistry, X-ray diffraction, Hydroformylation