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Heterobimetallic Complexes of Palladium with Mercury, Silver, Rhodium, Iridium or Molybdenum Containing $Ph_2PCH_2PPh_2$ (dppm)

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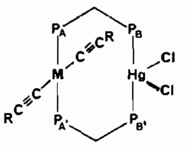
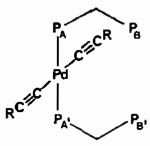
Introduction

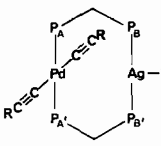
We have described previously, simple, high yielding, routes to complexes of type *trans*-$[Pt(C{\equiv}CR)_2(\eta^1\text{-dppm})_2]$ (dppm = $Ph_2PCH_2PPh_2$) (R = alkyl or aryl), such as the treatment of $[PtCl_2\ (\eta^2\text{-dppm})]$ with $LiC{\equiv}CR$ to give $[Pt_2(C{\equiv}CR)_4(\mu\text{-dppm})_2]$ followed by the addition of dppm [1]. Subsequently these η^1-dppm complexes were converted into heterobimetallic complexes with other metals such as Rh, Ir, Ag, Au, Cd, Hg or W [2, 3]. However, similar attempts to make palladium complexes, *trans*-$[Pd(C{\equiv}CR)_2(\eta^1\text{-dppm})_2]$ were completely unsuccessful, dark brown decomposition products being obtained. We have now found a simple, reliable method of synthesizing palladium complexes of type *trans*-$[Pd(C{\equiv}CR)_2(\eta^1\text{-dppm})_2]$ which we have then used to synthesize heterobimetallic complexes, either directly, or by transmetallation.

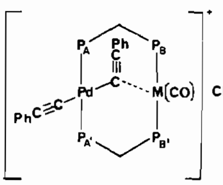
Results and Discussion

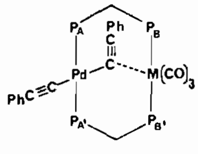
We have reported previously that treatment of $[Pt(\eta^2\text{-dppm})_2]2Cl$ with $Hg(C{\equiv}CR)_2$ gives (1a). We now find that treatment of a CD_2Cl_2 solution of $[Pd(\eta^2\text{-dppm})_2]2Cl$ {formed *in situ* from $[PdCl_2(\eta^2\text{-dppm})]$ + dppm} with $Hg(C{\equiv}CPh)_2$ at –40 °C gives the heterobimetalic complex (1b) in *ca.* 100% yield [from $^{31}P\text{-}\{^1H\}$ NMR evidence: δ_{P_A} = 19.2 ppm, δP_B = 23.0 ppm, $^1J(^{199}Hg\text{–}^{31}P_B)$ = 5678 Hz, $|^2J(P_AP_B) + {}^4J(P_AP_{B'})|$ = 82 Hz]. This complex decomposes at *ca.* +20 °C but when prepared in acetone–ethanol (1:1) at *ca.* –20 °C and then treated *in situ* with an equivalent amount of sodium sulphide in ethanol at or below 0 °C it gave mercuric sulphide and *trans*-$[Pd(C{\equiv}CPh)_2(\eta^1\text{-dppm})_2]$ (2a) in 85–90% isolated yields. This stable complex, which was fully characterized, is fluxional, showing an AA′XX′ $^{31}P\text{-}\{^1H\}$ NMR pattern at or below –60 °C but a broad singlet at +20 °C corresponding to rapid 'end over end' P_A/P_B intramolecular exchange. The *p*-tolyacetylide complex (2b) was made similarly (yield 52%). When treated with $[(Ph_3P)AgCl]_4$ in CH_2Cl_2 the η^1-dppm complex (2a) gave the palladium–silver complex (3a) in 98% isolated yield. This complex was characterized by elemental analysis (C, H, Cl) and by IR and NMR spectroscopy, *e.g.* the ^{31}P NMR data at –40 °C in CD_2Cl_2 where δP_A = 20.0 ppm, δP_B = –6.4 ppm, $^1J(^{107}Ag\text{–}P_B)$ = 398 Hz, $^1J(^{109}Ag\text{–}P_B)$ = 467 Hz, $|^2J(P_AP_B) + {}^4J(P_AP_{B'})|$ = 110 Hz; in the $^1H\text{-}\{^{31}P\}$ NMR spectrum, the coupling of the CH_2 protons to silver could be seen [$^3J(AgH)$ ~2.7 Hz] although the different values due to ^{107}Ag and ^{109}Ag were not resolved. The corresponding silver iodide complex (3b) was similarly made in 92% yield using $[(Ph_3P)AgI]_4$. We also find that treatment of $[Pd(C{\equiv}CPh)_2(\eta^1\text{-dppm})_2]$ (2a) with $[Rh_2Cl_2(CO)_4]$ in CH_2Cl_2 gives the orange salt $[(PhC{\equiv}C)_2Pd(\mu\text{-dppm})_2Rh(CO)]Cl$ (4a) in 85% yield. This complex (4a) is a 1:1 electrolyte in nitrobenzene and was characterized by elemental analysis (C, H and Cl) and by IR and ^1H and ^{31}P NMR spectroscopy. It is probable that one of the acetylide groups bridges both metals, as depicted in (4a) by analogy with the corresponding platinum complex [2]. Treatment of $[Pd(C{\equiv}CPh)_2(\eta^1\text{-dppm})_2]$ (2a) with $[Ir_2Cl_2(\text{cyclo-octene})_4]$, followed by CO gave the corresponding iridium salt (4b) which behaved as a 1:1 electrolyte in acetone. We have also attempted to form mixed palladium–tungsten or –molybdenum complexes by treating the η^1-dppm complex (2a) with $[W(CO)_3(NCMe)_3]$ or $[Mo(CO)_3(C_7H_8)]$ (C_7H_8 = cyclohepta-1,3,5-triene). No substantial amount of the desired mixed complexes could be detected by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy. However, treatment of the mixed palladium-silver complex (3a) with $[Mo(CO)_3(C_7H_8)]$ in CH_2Cl_2/CD_2Cl_2 gave the deep-red palladium–molybdenum complex (5a) in 80% isolated yield. This complex (5a) was character-


(1a) M = Pt ; R = Alkyl or aryl
(1b) M = Pd ; R = Ph


(2a) R = Ph
(2b) R = p-tolyl


(3a) X = Cl
(3b) X = I


(4a) M = Rh
(4b) M = Ir


(5a) M = Mo
(5b) M = W

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ized by elemental analysis, by IR spectroscopy (its IR spectrum was almost identical to that of the platinum–molybdenum analogue) and by NMR spectroscopy, *e.g.* its $^{31}P-\{^1H\}$ NMR spectrum showed $\delta P_A = 16.4$ ppm, $\delta P_B = 38.7$ ppm and $|^2J(P_AP_B) + {}^4J(P_AP_{B'})| = 87$ Hz. A $^{31}P-\{^1H\}$ NMR experiment showed that the conversion of (3a) to (5a), by transmetallation, following treatment of (3a) with $[Mo(CO)_3(C_7H_8)]$ was *ca.* 100% and no other phosphorus-containing species could be detected. Treatment of (3a) with *fac*-$[W(CO)_3(NCMe)_3]$ in CH_2Cl_2/CD_2Cl_2 gave some of the palladium–tungsten analogue (5b) [$^{31}P-\{^1H\}$ NMR evidence] but the conversion was slow and pure (5b) has not yet been isolated. The palladium–rhodium complex (4a) was readily formed by transmetallation, using either the palladium–silver complex (3a) or the palladium–mercury complex (1b) (prepared *in situ* at −20 °C): these complexes were treated with $[Rh_2Cl_2(CO)_4]$ in CH_2Cl_2/CD_2Cl_2, the progress of the conversion being followed by $^{31}P-\{^1H\}$ NMR spectroscopy.

Acknowledgements

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References

1 P. G. Pringle and B. L. Shaw, *J. Chem. Soc., Chem. Commun.,* 581 (1982).
2 D. M. McEwan, P. G. Pringle and B. L. Shaw, *J. Chem. Soc., Chem. Commun.,* 859 (1982).
3 W. S. McDonald, P. G. Pringle and B. L. Shaw, *J. Chem. Soc., Chem. Commun.,* 861 (1982).