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Facile transmetalation of a pyridyl-phosphine ligand from ruthenium to gold and silver

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ABSTRACT

Treatment of $[RuCl_2(\eta^6\text{-}p\text{-cymene})\{\kappa^1\text{-}(P)\text{-}PPh_2(py\text{-}6\text{-}tert\text{-}amyl)\}]$ (**1a**) and $[RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})\{\kappa^1\text{-}(P)\text{-}PPh_2(py\text{-}6\text{-}tert\text{-}amyl)\}]$ (**1b**) with $[AuCl(SMe_2)]$, in dichloromethane at room temperature, resulted in the formation of the dimethyl sulfide adducts $[RuCl_2(\eta^6\text{-}p\text{-cymene})(SMe_2)]$ (**3a**) and $[RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(SMe_2)]$ (**3b**), and the Au(I) complex $[AuCl\{\kappa^1\text{-}(P)\text{-}PPh_2(py\text{-}6\text{-}tert\text{-}amyl)\}]$ (**4**). Transmetalation of the pyridyl-phosphine $PPh_2(py\text{-}6\text{-}tert\text{-}amyl)$ (**2**) was also observed when dichloromethane solutions of **1a**–**b** were treated with $AgSbF_6$ in the presence of SMe_2, the reactions leading to **3a**–**b** and the dinuclear Ag(I) derivative $[Ag_2\{\mu\text{-}PPh_2(py\text{-}6\text{-}tert\text{-}amyl)\}_2][SbF_6]_2$ (**5**). In the absence of SMe_2 transmetalation of the phosphine to silver was not observed. Instead, the unexpected protonation of the pyridyl group by HF, generated by partial hydrolysis of the SbF_6^- anion, occurred. Compounds $[AuCl\{\kappa^1\text{-}(P)\text{-}PPh_2(py\text{-}6\text{-}tert\text{-}amyl)\}]$ (**4**) and $[Ag_2\{\mu\text{-}PPh_2(py\text{-}6\text{-}tert\text{-}amyl)\}_2][SbF_6]_2$ (**5**) were independently synthesized by reacting **2** with $[AuCl(SMe_2)]$ and $AgSbF_6$, respectively, and their structures confirmed by means of single-crystal X-ray diffraction techniques, along with those of the protonated species $[RuCl_2(\eta^6\text{-}p\text{-cymene})\{\kappa^1\text{-}(P)\text{-}PPh_2(pyH\text{-}6\text{-}tert\text{-}amyl)\}][SbF_6]$ (**6a**) and $[RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})\{\kappa^1\text{-}(P)\text{-}PPh_2(pyH\text{-}6\text{-}tert\text{-}amyl)\}][SbF_6]$ (**6b**).

1. Introduction

Heteroditopic (2-pyridyl)-phosphines are versatile and easily tunable ligands which can coordinate to metal fragments in monodentate, chelate or bridge form, depending on the requirements at the metal centre (Fig. 1) [1]. Owing to the different properties of the *P*- and *N*-donor groups, they also represent typical examples of hemilabile ligands able to reversibly undergo chelate ring-opening processes [2]. In this way, a coordination site can be temporarily liberated for substrate binding, a property that has been widely exploited in the stoichiometric and catalytic chemistry of many transition-metals [1].

The ability of the nitrogen atom of the pyridyl unit to establish hydrogen bonds, or to participate in proton transfer processes, has also been tapped for the development of new "bifunctional catalysts" based on metal complexes with κ^1-(*P*)-coordinated pyridyl-phosphines [3]. Pioneering reports by Grotjahn and co-workers of enhanced activities and selectivities in the ruthenium-catalyzed *anti*-Markovnikov hydration of alkynes [4] have stimulated an intense research in this field [3]. Related works by Oshiki and co-workers have also demonstrated the high potential of pyridyl-phosphines for the design of effective bifunctional catalysts for nitrile hydration reactions [5]. In this context, and in line with our current studies on this catalytic transformation [6], we have recently described the catalytic behaviour of the novel arene-ruthenium(II) and bis(allyl)-ruthenium(IV) derivatives $[RuCl_2(\eta^6\text{-}p\text{-cymene})\{\kappa^1\text{-}(P)\text{-}PPh_2(py\text{-}6\text{-}tert\text{-}amyl)\}]$ (**1a**) and $[RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})\{\kappa^1\text{-}(P)\text{-}PPh_2(py\text{-}6\text{-}tert\text{-}amyl)\}]$ (**1b**) ($C_{10}H_{16}$ = 2,7-dimethylocta-2,6-diene-1,8-diyl) [7]. A remarkable property of these complexes, which were readily prepared through classical chloride bridges-splitting reactions of the dimeric precursors $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}p\text{-cymene})\}_2]$ and $[\{RuCl(\mu\text{-}Cl)(\eta^3{:}\eta^3\text{-}C_{10}H_{16})\}_2]$ with the commercially available 2-(diphenylphosphino)pyridine ligand $PPh_2(py\text{-}6\text{-}tert\text{-}amyl)$ (**2**) [8], is the fact that they do not form the corresponding cationic chelate species $[RuCl(\eta^6\text{-}p\text{-cymene})\{\kappa^2\text{-}(P,N)\text{-}PPh_2(py\text{-}6\text{-}tert\text{-}amyl)\}]^+$ and $[RuCl(\eta^3{:}\eta^3\text{-}C_{10}H_{16})\{\kappa^2\text{-}(P,N)\text{-}PPh_2(py\text{-}6\text{-}tert\text{-}amyl)\}]^+$, even in the presence of a chloride abstractor such as $NaSbF_6$ [7]. Steric hindrance between the bulky *tert*-amyl substituent adjacent to the nitrogen atom and the coordinated *p*-cymene or 2,7-dimethylocta-2,6-diene-1,8-diyl ligands is behind this behaviour.

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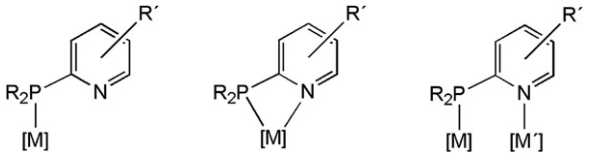


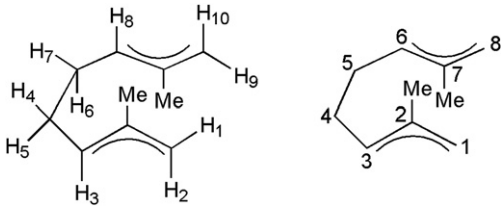
Fig. 1. The most common coordination modes of (2-pyridyl)-phosphine ligands.

The reluctance of PPh_2(py-6-*tert*-amyl) (**2**) to adopt a chelating κ^2-(*P*,*N*) coordination mode in these systems prompted us to study the reactivity of complexes **1a**–**b** towards [AuCl(SMe_2)], as a potential entry for the preparation of unprecedented heterobimetallic Ru/Au derivatives bridged by a (2-pyridyl)-phosphine ligand [9]. Although this goal could not be achieved, as the reader will see in this article, a series of unusual transmetalation processes have been disclosed throughout our study.

2. Experimental

2.1. General information

All manipulations were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen before use. All reagents were obtained from commercial suppliers and used without further purification, with the exception of compounds [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$] [10], [{RuCl(μ-Cl)(η^3:η^3-$C_{10}H_{16}$)}$_2$] [11], [$RuCl_2$(η^6-*p*-cymene){κ^1-(*P*)-PPh_2(py-6-*tert*-amyl)}] (**1a**) [7], [$RuCl_2$(η^3:η^3-$C_{10}H_{16}$){κ^1-(*P*)-PPh_2(py-6-*tert*-amyl)}] (**1b**) [7], [AuCl(SMe_2)] [12] and [$RuCl_2$(η^6-*p*-cymene)(SMe_2)] (**3a**) [13], which were prepared by following the methods reported in the literature. The C, H, and N analyses were carried out with a Perkin–Elmer 2400 microanalyzer. NMR spectra were recorded on Bruker DPX300 or AV400 instruments. Chemical shifts are given in ppm, relative to internal tetramethylsilane (^{1}H and ^{13}C), and external 85% aqueous H_3PO_4 solutions (^{31}P). DEPT experiments have been carried out for all the compounds reported in this paper. The numbering for protons and carbons of the 2,7-dimethylocta-2,6-diene-1,8-diyl skeleton is as follows:



2.2. Reactions of complexes [$RuCl_2$(η^6-*p*-cymene){κ^1-(*P*)-PPh_2(py-6-*tert*-amyl)}] (**1a**) and [$RuCl_2$(η^3:η^3-$C_{10}H_{16}$){κ^1-(*P*)-PPh_2(py-6-*tert*-amyl)}] (**1b**) with [AuCl(SMe_2)]

A solution of the corresponding ruthenium complex **1a**–**b** (1 mmol) in dichloromethane (10 mL) was treated with [AuCl(SMe_2)] (0.294 g, 1 mmol) at room temperature for 48 (**1a**) or 12 h (**1b**). The solvent was then removed under vacuum to give an orange solid residue. The ^{31}P{^{1}H} and ^{1}H NMR spectra ($CDCl_3$) of this solid indicated the presence of a mixture containing the Au(I) complex [AuCl{κ^1-(*P*)-PPh_2(py-6-*tert*-amyl)}] (**4**) and the corresponding dimethyl sulfide adduct [$RuCl_2$(η^6-*p*-cymene)(SMe_2)] (**3a**) or [$RuCl_2$(η^3:η^3-$C_{10}H_{16}$)(SMe_2)] (**3b**), along with a minor amount of the corresponding ruthenium dimer [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$] or [{RuCl(μ-Cl)(η^3:η^3-$C_{10}H_{16}$)}$_2$]. Complex **4** could be isolated from these mixtures, as a white solid, by chromatographic purification over silica gel using dichloromethane as eluent (*ca.* 0.300 g; 53% yield). In contrast, all attempts to isolate complexes **3a**–**b** by column chromatography failed. Thus, although further elution with a dichloromethane/methanol (2/1) mixture gave rise, in both cases, to a new brown band, their ^{1}H NMR spectra ($CDCl_3$) showed a complex mixture of decomposition products. Characterization data for complex [AuCl{κ^1-(*P*)-PPh_2(py-6-*tert*-amyl)}] (**4**) are as follows: ^{31}P{^{1}H} NMR (CD_2Cl_2): δ = 31.3 (s) ppm; ^{1}H NMR (CD_2Cl_2): δ = 0.60 (t, $^3J_{HH}$ = 7.5 Hz, 3H, CH_2CH_3), 1.27 (s, 6H, $C(CH_3)_2$), 1.68 (q, $^3J_{HH}$ = 7.5 Hz, 2H, CH_2CH_3), 7.42–7.58 (m, 6H, CH_{arom}), 7.72–7.96 (m, 7H, CH_{arom}) ppm; ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 8.8 (s, CH_2CH_3), 26.9 (s, $C(CH_3)_2$), 35.6 (s, CH_2CH_3), 41.2 (s, $C(CH_3)_2$), 122.1 (d, $^2J_{PC}$ = 2.4 Hz, CH_{arom}), 128.7 (d, $^3J_{PC}$ = 11.8 Hz, CH_{arom}), 129.1 (s, CH_{arom}), 129.4 (d, $^1J_{PC}$ = 63.5 Hz, C_{arom}), 131.7 (d, $^4J_{PC}$ = 2.6 Hz, CH_{arom}), 134.5 (d, $^2J_{PC}$ = 13.3 Hz, CH_{arom}), 136.7 (d, $^3J_{PC}$ = 11.8 Hz, CH_{arom}), 151.8 (d, $^1J_{PC}$ = 86.6 Hz, C_{arom}), 169.9 (d, $^3J_{PC}$ = 14.2 Hz, C_{arom}) ppm; Anal. Calcd for $AuC_{22}H_{24}ClNP$ (565.83 g/mol): C, 46.70; H, 4.28; N, 2.48. Found: C, 46.57; H, 4.23; N, 2.32%.

2.3. Synthesis of complex [$RuCl_2$(η^3:η^3-$C_{10}H_{16}$)(SMe_2)] (**3b**)

A solution of the dimeric precursor [{RuCl(μ-Cl)(η^3:η^3-$C_{10}H_{16}$)}$_2$] (0.100 g, 0.16 mmol) in dichloromethane (10 mL) was treated with dimethyl sulfide (24 μL, 0.33 mmol) at room temperature for 15 min (the solution turned from violet to orange within a few minutes) and then evaporated to dryness. The resulting orange solid residue was washed with hexanes (5 mL) and vacuum-dried. Yield: 95% (0.113 g); ^{1}H NMR (CD_2Cl_2): δ = 2.32 and 2.35 (s, 6H each, CH_3 and $S(CH_3)_2$), 2.62 (m, 2H, H_4 and H_6), 3.94 (m, 2H, H_5 and H_7), 3.81 (s, 2H, H_2 and H_{10}), 4.59 (s, 2H, H_1 and H_9), 4.90 (m, 2H, H_3 and H_8) ppm; ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 20.2 and 21.9 (s, CH_3 and $S(CH_3)_2$), 35.3 (s, C_4 and C_5), 74.1 (s, C_1 and C_8), 99.4 (s, C_3 and C_6), 125.8 (s, C_2 and C_7) ppm; Anal. Calcd for $RuC_{12}H_{22}Cl_2S$ (370.34 g/mol): C, 38.92; H, 5.99. Found: C, 38.98; H, 6.02%.

2.4. Synthesis of complex [AuCl{κ^1-(*P*)-PPh_2(py-6-*tert*-amyl)}] (**4**) starting from [AuCl(SMe_2)] and PPh_2(py-6-*tert*-amyl) (**2**)

A solution of [AuCl(SMe_2)] (0.088 g, 0.3 mmol) in dichloromethane (10 mL) was treated with the phosphine ligand **2** (0.100 g, 0.3 mmol) at room temperature for 1 h, and then concentrated to *ca.* 3 mL. Addition of hexanes (30 mL) led to the precipitation of a white solid, which was washed with hexanes (5 mL) and vacuum-dried. Yield: 91% (0.154 g).

2.5. Reactions of complexes [$RuCl_2$(η^6-*p*-cymene){κ^1-(*P*)-PPh_2(py-6-*tert*-amyl)}] (**1a**) and [$RuCl_2$(η^3:η^3-$C_{10}H_{16}$){κ^1-(*P*)-PPh_2(py-6-*tert*-amyl)}] (**1b**) with $AgSbF_6$ in the presence of SMe_2

To a solution of the corresponding ruthenium–phosphine complex **1a**–**b** (1 mmol) in dichloromethane (10 mL) were added SMe_2 (734 μL, 10 mmol) and $AgSbF_6$ (0.343 g, 1 mmol), and the resulting mixture stirred at room temperature, and in the absence of light, for 48 (**1a**) or 12 h (**1b**). The volatiles were then removed under vacuum to give a brown solid residue. The ^{31}P{^{1}H} and ^{1}H NMR spectra ($CDCl_3$) of this solid indicated the presence of a mixture containing the dinuclear Ag(I) complex [Ag_2\{μ-PPh_2(py-6-*tert*-amyl)}$_2$][SbF_6]$_2$ (**5**) and the corresponding dimethyl sulfide adduct [$RuCl_2$(η^6-*p*-cymene)(SMe_2)] (**3a**) or [$RuCl_2$(η^3:η^3-$C_{10}H_{16}$)(SMe_2)] (**3b**), along with a minor amount of the corresponding ruthenium dimer [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$] or [{RuCl(μ-Cl)(η^3:η^3-$C_{10}H_{16}$)}$_2$]. Complex **5** could be isolated in pure form, as a white solid, from these mixtures by successive recrystallizations from dichloromethane–diethyl ether (*ca.* 0.450 g; 66% yield). Characterization data for [Ag_2\{μ-PPh_2(py-6-*tert*-amyl)}$_2$][SbF_6]$_2$ (**5**) are as