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Effect of trimethylsilyl substitution on the chemical properties of triarylphosphines and their corresponding metal-complexes: solubilising effect in supercritical carbon dioxide[†]

Francisco Montilla,*ª Agustín Galindo,ª Vitor Rosa^b and Teresa Avilés^b

^a Departamento de Química Inorgánica, Facultad de Química, Universidad de Sevilla, Aptdo. 553, 41071 Sevilla. E-mail: montilla@us.es

^b REQUIMTE/CQFB, Departamento de Química, FCT, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal

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The donor strengths of the following triarylphosphine ligands $P(Ar)_2(Ar')$ ($Ar = Ar' = 4-Me_3SiC_6H_4$, **1b**; $4-Me_3CC_6H_4$, **1c**; $Ar = C_6H_5$, $Ar' = 4-Me_3SiC_6H_4$, **1c**) have been evaluated experimentally and theoretically. The measurements of the *J*(P–Se) coupling constants of the corresponding synthesised selenides $Se=P(Ar)_2(Ar')$, **2b**, **c** and the DFT calculation of the energies of the phosphine lone-pair (HOMO) reveal insignificant influence on the electronic properties of the substituted phosphines when the trimethylsilyl group is attached to the aryl ring, in marked contrast to the strong electronic effect of the trifluoromethyl group. These triarylphosphine ligands $P(Ar)_2(Ar')$ reacted with ($\eta^5-C_5H_5$)Co(CO)₂, ($\eta^5-C_5H_5$)Co(CO)I₂ or PdCl₂ to yield the new compounds ($\eta^5-C_5H_5$)Co(CO)[P(Ar)₂(Ar')], **3b**,d; ($\eta^5-C_5H_5$)CoI₂[P(Ar)₂(Ar')], **4b**–e; and PdCl₂[P(Ar)₂(Ar')]₂, **5b**,c, respectively. These complexes have been characterized and their spectroscopic properties compared with those reported for the known triphenylphosphine complexes. Again, the contrast of the ³¹P NMR and ¹³C NMR chemical shifts or C–O or M–Cl stretching frequencies, when applied, does not show an important electronic effect on the metal complex of the trimethylsilyl substituted phosphines with respect to $P(C_6H_5)_3$ derivatives. Solubility measurements of complexes **3a** and **3b** in scCO₂ were performed. We conclude that Me₃Si groups on the triarylphosphine improve the solubility of the corresponding metal complex in scCO₂.

Introduction

One of the important areas of development in metal mediated homogeneous catalysis is concerned with the use of nonconventional solvents such as water, room-temperature ionic liquids (RTIL), supercritical carbon dioxide (scCO₂), and perfluorocarbons, as reaction media.1 Triphenylphosphine is a widely used ligand in homogeneous catalysis,² but the phosphine itself and their complexes are not particularly soluble in those solvents. Therefore, the use of related ligands containing solubilising groups attached to the aryl phosphine substituents has been a widely applied strategy in the past few years in order to improve the solubility of metal complexes. For catalysis in highly polar media (i.e. aqueous phase or RTIL), this can be done by appending the arylphosphines with hydrophilic groups such as -SO₃Na, -CO₂Na and -NR₃Cl,^{3,4} whereas by attaching perfluorinated moieties to the arylphosphines results in metal-complexes that are fluorous-soluble or scCO₂soluble.5,6 The latter strategy has been successfully applied to a wide range of scCO₂ metal catalysed homogeneous processes.⁷⁻⁹ A possible drawback to their more generalized use is the strong electron-withdrawing properties of the fluoroalkyl groups that affect the reactivity of the catalyst.9 A successful solution to this problem was found by using an appropriate spacer.¹⁰ In any case, the synthesis of ligands of this sort, as well as of their metal complexes, is usually difficult and expensive. For these reasons, the design of new solubilisers, that are easy to prepare but do not alter the chemical properties of the catalyst, is a highly desirable goal.

With respect to this, we have recently reported a new methodology that increases the solubility of cyclopentadienyl metal complexes in $scCO_2$ through the functionalisation of the Cp ligand with one trimethylsilyl group (TMS).¹¹ We are currently investigating the effect of introducing a TMS on several ligands and here we report the extension of our studies to triphenylphosphine. Initially, we examined the σ -donor ability of the free phosphine ligands, both

† Electronic supplementary information (ESI) available: selected computed data of the arylphosphines and correlations between their computed HOMO energies and spectroscopic parameters of the corresponding selenides. See http://www.rsc.org/suppdata/dt/b4/b406691j/ experimentally and theoretically. Subsequently, we prepared several new cobalt and palladium complexes and studied the effect of TMS substitution on the basis of the comparison of their spectroscopic properties with those of the parent, non-substituted, $P(C_6H_5)_3$ -metal complexes and, additionally, *tert*-butyl or trifluoromethyl substituted triphenylphosphine metal complexes. Finally, we have verified how the TMS functionalization of the triphenylphosphine ligand increases the solubility of the metal complexes in the scCO₂ media.

Experimental

All preparations and other operations were carried out under dry oxygen-free nitrogen or argon atmosphere following conventional Schlenk techniques. Solvents were dried and degassed before Tris(4-trimethylsilylphenyl)phosphine, $P(4-Me_3SiC_6H_4)_3$ use. (**1b**)¹² and diphenyl(4-trimethylsilylphenyl)phosphine, P(4- $Me_3SiC_6H_4)(C_6H_5)_2$ (1c)¹³ were prepared, according to previously described procedures, through the reaction of the appropriate aryl magnesium bromide with phosphorus trichloride or (C₆H₅)₂PCl, respectively. Phosphines $P(4-Me_3CC_6H_4)_3$ (1d)¹⁴ and $P(4-Me_3CC_6H_4)_3$ $F_3CC_6H_4)_3$ (1e)¹⁵ and compounds ($\eta^5-C_5H_5$)Co(CO)₂¹⁶ and ($\eta^5-C_5H_5$)Co(CO)₂ C_5H_5)Co(CO)I₂¹⁷ were also prepared by the methods reported in the literature. CO₂, employed for supercritical measurements, was purchased from Carburos Metálicos (99.9999% purity). Infrared spectra were recorded on Perkin-Elmer Model 883 and ATI Mattson Genesis FTIR spectrophotometer. ¹H, ¹³C and ³¹P NMR spectra were run on Bruker AMX-300, Bruker AMX-500 or Bruker ARX-400 spectrometer. ¹H NMR spectra were recorded using SiMe₄ as internal reference, and ¹³C NMR spectra were referenced using the ¹³C resonance of the solvent as internal standard. ³¹P shifts were measured with respect to external 85% H₃PO₄. Microanalyses (C, H, N) were carried out by the Microanalytical Service of the University of Sevilla (Spain) or by the Microanalytical Laboratory of the Universidade Técnica de Lisboa (Portugal).

Preparation of phosphine selenides 2

The known derivatives $2a^{18}$ and $2e^{19}$ were prepared as previously reported by heating a solution in toluene of the corresponding

2588

phosphine in contact with elemental selenium. The new phosphine selenide compounds 2b and 2c were similarly obtained, as described below for 2b

 $Se=P(4-Me_3SiC_6H_4)_3$, 2b. A solution of 1b (0.026 g, 0.054 mmol) in toluene (1 ml) was heated at 110 °C in the presence of elemental selenium (0.02 g, 0.26 mmol, excess) for three days. The resulting yellow solution was filtered and the volatiles were removed under vacuum. Compound 2b was obtained as an air-sensitive yellow solid. Analysis by ³¹P NMR indicated that the reaction was complete. ¹H NMR (C_6D_6): δ 7.91 (m, 6, Ar), 7.26 (m, 6, Ar), 0.12 (s, 27, Si(CH₃)₃). ${}^{13}C{}^{1}H{}$ NMR (C₆D₆): δ 144.51–131.34 (Ar), -1.72 (s, Si(CH₃)₃). ³¹P NMR (C₆D₆): δ 34.62 $({}^{1}J_{\rm PSe} = 758 \text{ Hz}).$

 $Se = P(4-Me_3SiC_6H_4)(C_6H_4)_2$, 2c. ¹H NMR (C₆D₆): δ 7.85–6.94 (m, 14, Ar), 0.11 (s, 9, Si(CH₃)₃). ${}^{13}C{}^{1}H{}^{1}$ NMR (C₆D₆): δ 144.22-130.98 (Ar), -1.74 (s, Si(CH₃)₃). ³¹P NMR (C₆D₆): δ 34.65 $({}^{1}J_{\rm PSe} = 758 \text{ Hz}).$

Synthesis of (η⁵-C₅H₅)Co(CO)(phosphine) complexes 3

Carbonyl-cobalt complexes were prepared by reacting (η^5 - C_5H_5)Co(CO)₂ with the appropriate phosphine as described below for **3b**. The preparation of $(\eta^5-C_5H_5)Co(CO)[(P(C_6H_5)_3]$ **3a** has already been reported.20

 $(\eta^{5}-C_{5}H_{5})Co(CO)[P(4-Me_{3}SiC_{6}H_{4})_{3}]$, 3b. A mixture of $(\eta^{5}-C_{5}H_{5})CO(CO)[P(4-Me_{3}H_{5})CO(CO)]$ C₅H₅)Co(CO)₂ (0.353 g, 1.96 mmol) and 1b (0.94 g, 1.96 mmol) in 60 ml of petroleum ether (boiling range 100-140 °C) was kept under reflux for 24 h. The resulting red-black reaction mixture was cooled to room temperature, a red crystalline solid precipitating out of the solution. After several hours the mixture was filtered and the resulting crystals were washed with portions of petroleum ether (boiling range 40-60 °C) and air-sensitive red crystals of compound **3b** were obtained (0.9 g, 72%). ¹H NMR (C_6D_6): δ 7.93 (m, 6, Ar), 7.46 (m, 6, Ar), 4.81 (s, 5, Cp), 0.25 (s, 27, Si(CH₃)₃). ¹³C{¹H} NMR (C₆D₆): δ 208.16 (br, CO), 142.24–133.22 (Ar), 83.11 (s, Cp), -1.28 (s, Si(CH₃)₃). ³¹P NMR (C₆D₆): δ 69.32 (s). IR (Nujol): ν/cm⁻¹ 1924 (M-CO). Elemental analysis (found: C, 61.90; H, 7.63: calc. for C₃₃H₄₄OPSi₃Co: C, 62.83; H, 7.03%).

 $(\eta^{5}-C_{5}H_{5})Co(CO)[P(4-Me_{3}CC_{6}H_{4})_{3}]$, 3d. A mixture of $(\eta^{5}-C_{5}H_{5})Co(CO)[P(4-Me_{3}CC_{6}H_{4})_{3}]$ C₅H₅)Co(CO)₂ (0.3 g, 1.6 mmol) and 1d (0.7 g, 1.6 mmol) in 60 ml of petroleum ether (boiling range 100-140 °C) was treated as before in 3b. Compound 3d was obtained as air-sensitive red crystals (0.56 g, 60%). ¹H NMR (C₆D₆): δ 7.85 (s, 4, Ar), 4.77 (s, 5, Cp), 1.20 (s, 27, C(CH₃)₃). ${}^{13}C{}^{1}H{}$ NMR (C₆D₆): δ 209.67 (br, CO), 153.37, 136.01–135.56, 134.64, 125.77 (Ar), 83.47 (Cp), 34.77 (s, C(CH₃)₃), 31.32 (s, C(CH₃)₃). ³¹P NMR (C₆D₆): δ 66.09 (s). IR (Nujol): $v/cm^{-1} = 1924$ (M–CO). Elemental analysis (found: C, 74.02; H, 7.70: calc. for C₃₆H₄₄OPCo: C, 74.21; H, 7.61%).

Synthesis of (η⁵-C₅H₅)CoI₂(phosphine) complexes 4

Diiodo-cobalt complexes were prepared by reacting $(\eta^5-C_5H_5)CoI_2$ -(CO) with the appropriate phosphine as described below for 4b. The synthesis of complex $(\eta^5-C_5H_5)Co[(P(C_6H_5)_3]I_2$ 4a has already been described.17

 $(\eta^{5}-C_{5}H_{5})CoI_{2}[P(4-Me_{3}SiC_{6}H_{4})_{3}]$, 4b. A solution of $(\eta^{5}-C_{5}H_{5})CoI_{2}[P(4-Me_{3}SiC_{6}H_{4})_{3}]$, C₅H₅)Co(CO)I₂ (0.85 g, 2.09 mmol) in 40 ml of dichloromethane was added slowly at r.t. to a stirred solution of $P(4-Me_3SiC_6H_4)_3$ (1 g, 2.09 mmol) in 30 ml of dichloromethane. Rapid gas evolution occurred and the original dark purple colour of $(\eta^5-C_5H_5)Co(CO)I_2$ became dark green. After stirring overnight at room temperature, the reaction mixture was filtered and 5 ml of petroleum ether was added to the filtrate. The solvent was gradually removed under vacuum until precipitation of the dark green crystals appeared to be complete. The product was then filtered, washed with diethyl ether and petroleum ether, and dried to give dark green crystals of 4b (1 g,

56%). ¹H NMR (CDCl₃): δ 8.10–8.05 (m, 6, Ar), 7.40 (s, H, Ar), 4.75 (s, 5 H, Cp), 0.21 (s, 27, Si(CH₃)₃). ${}^{13}C{}^{1}H{}$ NMR (CDCl₃): δ 144.61, 134.69, 134.05 (s, Ar), 87.48 (s, Cp), -0.66 (Si(CH₃)₃). ³¹P NMR (CDCl₃): δ 31.01 (s). Elemental analysis (found: C, 44.91; H, 5.01: calc. for C₃₂H₄₄PSi₃CoI₂: C, 44.87; H, 5.18%).

 $(\eta^{5}-C_{5}H_{5})CoI_{2}[P(4-Me_{3}SiC_{6}H_{4})(C_{6}H_{5})_{2}], 4c. A mixture of (\eta^{5}-$ C5H5)Co(CO)I2 (0.65 g, 1.6 mmol) and P(4-Me3SiC6H4)(C6H4)2 (0.19 g, 1.6 mmol) in 60 ml of CH₂Cl₂ was treated as described above. Compound 4c was obtained as dark green crystals (0.21 g, 18%). ¹H NMR (C₆D₆): δ 8.02–7.98 (m, 7, Ar), 7.41–7.11 (m, 7, Ar), 4,71 (s, 5, Cp), 0.15 (s, 9, Si(CH₃)₃). ¹³C NMR (100 MHz, C₆D₆): δ 134.74, 134.67 (d, Ar) 134.04, 133.96 (d, Ar), 130.91 (s, Ar), 86.89 (s, Cp), -1.26 (s, CH₃). ³¹P NMR (C₆D₆): δ 30.80. Elemental analysis (found: C, 44.03; H, 3.88: calc. for C₂₆H₂₈PSiCoI₂: C, 43.84; H, 3 96%)

 $(\eta^{5}-C_{5}H_{5})CoI_{2}[P(4-Me_{3}CC_{6}H_{4})_{3}], 4d.$ A solution of $(\eta^{5}-C_{5}H_{5})CoI_{2}[P(4-Me_{3}CC_{6}H_{4})_{3}], 4d.$ C₅H₅)Co(CO)I₂ (0.18 g, 0.4 mmol) and P(4-Me₃CC₆H₄)₃ (0.19 g, 0.4 mmol) in 60 ml of CH₂Cl₂ was treated as mentioned above. Compound 4d was obtained as dark green crystals (0.16 g, 56%). ¹H NMR (CDCl₃): δ 8.30 (s, 12, Ar), 5.04 (s, 5, Cp), 1.18 (s, 27, $C(CH_3)_3$). ¹³C{¹H} NMR (CDCl₃): δ 155.33, 133.25, 132.12 (s, Ar), 85.08 (s, Cp), 32.35 (C(CH₃)₃), 29.28 (C(CH₃)₃). ³¹P NMR (CDCl₃): δ 27.71 (s). Elemental analysis (found: C 52.05, H 5.61: calc. for C₃₅H₄₄CoI₂P: C 52.00 H 5.49%).

(η⁵-C₅H₅)CoI₂[P(4-F₃CC₆H₄)₃], 4e. A solution of (η⁵-C₅H₅)Co-(CO)I₂ (0.52 g, 1.3 mmol) and P(4-F₃CC₆H₄)₃ (0.5 g, 1.3 mmol) in 60 ml of CH₂Cl₂ was treated as stated above. Compound 4e was obtained as dark green crystals (0.74 g, 68%). ¹H NMR (CDCl₃): δ 8.01–7.79 (m, 12, Ar), 5.15 (s, 5, Cp). ¹³C{¹H} NMR (CDCl₃): δ 134.65, 132.74, 125.98 (s, Ar), 87.10 (s, Cp). ³¹P NMR (C₆D₆): δ 32.1 (s). Elemental analysis (found: C, 38.10; H, 2.04: calc. for C₂₆H₁₇PF₉CoI₂: C, 37.00; H, 2.03%).

Synthesis of PdCl₂(phosphine)₂ complexes 5

Palladium complexes $5a^{21}$ and $5e^{22}$ were prepared as reported in the literature by reacting a solution of the corresponding phosphine in ethanol with PdCl₂. The new phosphine-palladium compounds 5b and 5c were prepared by the same method.

PdCl₂[P(4-Me₃SiC₆H₄)₃]₂, 5b. A mixture of 1b (0.22 g, 0.47 mmol) and PdCl₂ (0.042 g, 0.24 mmol) were mixed in ethanol (25 ml) at 40 °C for 72 h. A long reaction time was required due to the low solubility of reagents in the solvent. The resulting suspension was filtered off and the yellow solid washed with petroleum ether in order to eliminate the unreacted phosphine. Compound 5b was obtained as a yellow solid (0.18 g, 66%). ¹H NMR (CDCl₃): δ 7.67, 7.52 (m, 6, Ar), 0.26 (s, 27, Si(CH₃)₃). ¹³C{¹H} NMR (CDCl₃): δ 143.54, 134.27, 133.01, 130.12 (s, Ar), -1.06 (s, Si(CH₃)₃). ³¹P NMR (CDCl₃): δ 22.25 (s). IR (Nujol): v/cm⁻¹ 360 (M–Cl). Elemental analysis (found: C, 56.35; H, 6.75: calc. for C₅₄H₇₈Cl₂Si₆P₂Pd: C, 57.14; H, 6.93%).

PdCl₂[P(4-Me₃SiC₆H₄)(C₆H₅)₂]₂, 5c. This compound was prepared as described above for 5b but using 1c (0.22 g, 0.66 mmol). The higher solubility of 1c in ethanol allowed the completion of the reaction in 2 h. Compound 5c was obtained as a yellow solid (0.22 g, 79%). ¹H NMR (CDCl₃): δ 7.70, 7.67 (m, 3H, Ar), 7.52 (d, ${}^{1}J_{\text{HH}} = 7.8$ Hz, 2H, Ar), 7.42 (m, 3H, Ar), 7.38 (t, ${}^{1}J_{\text{HH}} = 7.1$ Hz, 3H, Ar), 0.25 (s, 9, Si(CH₃)₃). ${}^{13}C{}^{1}H{}$ NMR (CDCl₃): δ 143.57, 135.053, 134.09, 132.87, 130.44, 128.02 (s, Ar), -1.27 (s, Si(CH₃)₃). ³¹P NMR (C₆D₆): δ 22.57 (s). IR (Nujol): $v/cm^{-1} = 356 (M-Cl).$

Experiments in supercritical CO₂: solubility measurements

A simple high-pressure apparatus, described elsewhere,11 was used to carry out the solubility measurements in scCO2. A view cell, with a volume of 11 ml and equipped with sapphire windows was used

Table 1	Synthesised compounds						
		$P(C_6H_5)_3$	$P(4-Me_3SiC_6H_4)_3$	$P(4-Me_3SiC_6H_4)(C_6H_5)_2$	$P(4-Me_3CC_6H_4)_3$	$P(4-F_3CC_6H_4)_3$	
	L	1a	1b	1c	1d	1e	
	Se=L	2a	2b	2c	_	2e	
	CpCo(CO)L	3a	3b	_	3d	_	
	CpCoI ₂ L	4a	4b	4c	4d	4e	
	PdCl ₂ L ₂	5a	5b	5c	—	5e	

for the experiments. Reagents were inserted into the cell under argon; the reactor was evacuated and then refilled with argon. The cell was subsequently placed in the high-pressure line and CO₂ is transferred into the cell by using a pneumatic liquid pump. The cell was heated to the desired temperature in a water-bath. A digital transducer measured the pressure. For each solubility measurement, a sufficient amount of compound was put into the view cell to give a saturated solution in scCO₂ at 40 °C and at the corresponding pressure. This was visually checked with the presence of the solid compound in the cell at the given pressure. Before performing any measurements, the mixtures were efficiently stirred for several hours in order to guarantee that the saturation of the complex in the supercritical phase had been achieved. Samples were taken through a high-pressure sample loop (0.5 ml), by filling it with the supercritical fluid mixture, depressurising it into a sample vial, and flushing it with CH₂Cl₂. Subsequently, the sample loop was dried with compressed air. The concentration of the CH2Cl2 solutions was determined by analysing them by UV spectroscopy.

Computational details

The electronic structure and geometries of the phosphine compounds **1a**, **1b**, **1c** and **1e** were computed within the density functional theory at the B3LYP^{23,24} level using the 6-31G+(d, p) basis set for all atoms. The optimised geometries of **1a** and **1c** were characterized as local energy minima by digitalisation of the analytically computed Hessian. In the frequency calculations of **1b** and **1e**, imaginary frequencies were obtained corresponding to the rotation of the TMS and CF₃ groups, around the C–Si and C–C bonds, respectively. In general, imaginary vibrational frequencies of small magnitude are problematic because recomputation sometimes does not produce changes in the results.²⁵ For this reason, and also because we assume that the HOMO energy, the parameter in which we are interested, would not change significantly after recomputation, no attempts to eliminate this frequency were performed. The DFT calculations were performed using the Gaussian 98 suite of programs.²⁶

Results and discussion

The aim of this work is to demonstrate that the introduction of one or several TMS groups on the 4-position of the phenyl group of triphenylphosphine produces an increase of the solubility of the corresponding metal complex in scCO₂, without significantly affecting its electronic properties. With this goal in mind, we selected several phosphines and prepared their corresponding selenides and new cobalt and palladium complexes containing these phosphines as ligands (Table 1). Two TMS-containing phosphines, P(4- $Me_3SiC_6H_4)_3$ **1b** and $P(C_6H_5)_2(4-Me_3SiC_6H_4)$ **1c**, were chosen and for comparative purposes, several of the parent, non-substituted, triphenylphosphine derivatives, a, were also synthesised. Furthermore, two other arylphosphines were selected, containing two completely different substituents, 4-tert-butyl and 4-trifluoromethyl, in terms of their donor-acceptor properties. Thus, compounds d and e (Table 1), respectively, were also prepared and characterised. Selected spectroscopic data (NMR and IR) of the corresponding metal compounds were studied for each series, which were used as indicators for electronic variations at the metal centre.

Donor strengths of free phosphine ligands

The effect produced upon formal substitution of the hydrogen atom on the 4-position of the phenyl ring of triphenylphosphine was
 Table 2
 ³¹P NMR data of phosphine selenide compounds

Compound ^a	J(P-Se)/Hz	$\delta(^{31}\text{P})/\text{ppm}$
$\begin{array}{l} Se = P(C_6H_5)_3 (\textbf{2a}) \\ Se = P(4-Me_3SiC_6H_4)_3 (\textbf{2b}) \\ Se = P(C_6H_5)_2(4-Me_3SiC_6H_4) (\textbf{2c}) \\ Se = P(4-F_3CC_6H_4)_3 (\textbf{2e}) \end{array}$	761 (733) ^b 758 758 785 (765) ^c	34.7 34.6 34.6 33.1
^a NMR in C ₂ D ₂ ^b Data taken from ref 1	8. ^c Data taken fror	n ref 19

studied by several groups. The first approach for estimating such an effect was the evaluation of the donor strength of the corresponding selected phosphines. This analysis was carried out from two complementary viewpoints: experimental and theoretical. On the experimental side, a simple way of evaluating the σ -donor ability of a phosphine is by measuring the magnitude of the coupling constant ${}^{1}J_{\text{SeP}}$ of the corresponding phosphine selenide.²⁷ To estimate the donor abilities of the arylphosphines **1b** and **1c**, we prepared the corresponding selenides **2b** and **2c** by reacting the phosphine with elemental selenium in toluene at 110 °C. In order to compare the spectroscopic data, we also prepared the known non-substituted **2a**¹⁸ and CF₃-substituted **2e**¹⁹ derivatives. Selenium satellites generated by the ⁷⁷Se isotopomers (7.6% natural abundance) are readily observed in the ³¹P NMR spectra (see Table 2).

The ${}^{1}J_{\text{SeP}}$ values of the TMS-substituted derivatives **2b** and **2c** are not much different from those of **2a** ($\Delta[{}^{1}J_{\text{SeP}}(2\mathbf{a}) - {}^{1}J_{\text{SeP}}(2\mathbf{b})] = 3$ Hz), which indicates only minor modification of the electronic properties of the phosphine selenide upon formal addition of the trimethylsilyl groups. However, these values are significantly lower than that of **2e** ($\Delta[{}^{1}J_{\text{SeP}}(2\mathbf{a}) - {}^{1}J_{\text{SeP}}(2\mathbf{e})] = 24$ Hz), in good agreement with the increased electron withdrawing character of the aryl substituent in the trifluoromethyl derivative. Similarly, the 31 P NMR chemical shifts of the selenide phosphine reflect the reduced chemical effect of the TMS group when attached to the arylphosphine, in comparison with the effect of the CF₃ group.

From the theoretical point of view, Senn and co-workers have recently shown, through DFT calculations, that there is a good correlation between the energy of the phosphine lone-pair (HOMO) and the donor strength of the ligand.²⁸ By using the same approach, we have calculated the HOMO energies of the following phosphines **1a**, **1b**, **1c** and **1e**. Their molecular structures (see ESI†) have been optimised at the same level of theory (B3LYP/6-31G+(d, p)) for an adequate comparison. The calculated structural parameters are in agreement with those experimentally found for $P(C_6H_5)_{3}^{29}$ and compares well with those observed in the few complexes containing coordinated $P(4-Me_3SiC_6H_4)_{3}^{10}$ and $P(4-F_3CC_6H_4)_{3}^{19,30}$. To our knowledge, no structural data are known for $P(C_6H_5)_2(4-Me_3SiC_6H_4)$.

Similar consequences to those obtained from ³¹P NMR of selenides can be derived from the calculated data. The donor strength of the TMS-containing phosphines **1b** and **1c** (measured by the HOMO energies, -5.95 and -5.98 eV, respectively) are close to that of P(C₆H₃)₃, **1a** (HOMO energy of -6.00 eV) and the formal H substitution by TMS introduced in the 4-position does not generate a noteworthy effect in the donor strength of the corresponding phosphine. By contrast, P(4-F₃CC₆H₄)₃, **1e**, shows an important stabilization of the HOMO (-6.89 eV) and subsequently a lower donor strength. Both, the experimental and the theoretical approaches are interrelated. In fact, a good correlation (R = 0.994) can be found when the coupling constant ¹J_{SeP} is compared with the energy of the lone pair (HOMO) and, additionally, an acceptable correlation

Table 3 Spectroscopy data of cobalt derivatives 3 and 4

	CpCo(CO)L, 3			$CpCoI_2L, 4$
Ligand, L	$\delta(^{31}\text{P})^a/\text{ppm}$	δ(¹³ C) (CO) ^{<i>a</i>} /ppm	v(CO)/cm ⁻¹	$\delta(^{31}\text{P})^b/\text{ppm}$
 $P(C_6H_5)_3$, a	70.0	208.7	1913	31.1
$P(4-Me_3SiC_6H_4)_3$, b $P(C_6H_5)_2(4-Me_3SiC_6H_4)$, c	69.3	208.2	1924	31.0 30.8
$P(4-Me_3CC_6H_4)_3, d$ $P(4-F_3CC_6H_4)_3, e$	66.1	209.7	1924	27.7 32.1

(R = 0.983) is obtained when the latter energy is compared with the ³¹P chemical shift of the selenide (see graphs in ESI†).

Synthesis of triarylphosphine metal complexes and their spectroscopic characterization

To ascertain the electronic properties of the TMS-containing phosphine ligands, their coordination and organometallic chemistry have been investigated through the preparation of several cobalt and palladium complexes. Selected spectroscopic properties of the latter compounds have been compared with that of the complexes containing the non-substituted, and the 'Bu- or CF_3 -substituted phosphines.

The cobalt complexes $(\eta^5-C_5H_5)Co(CO)[P(4-Me_3SiC_6H_4)_3]$, **3b**, $(\eta^5-C_5H_5)Co(CO)[P(4-Me_3CC_6H_4)_3]$, **3d**, were prepared by reaction of $[(\eta^5-C_5H_5)Co(CO)_2]$ with the corresponding phosphine, following an experimental procedure similar to that reported for compound $(\eta^5-C_5H_5)Co(CO)[P(C_6H_5)_3]$, **3a**.²⁰ Reaction of $[(\eta^5-C_5H_5)Co(CO)]$ C_5H_5)Co(CO)₂] with the trifluoromethylphosphine 1e did not afford isolable materials. Selected spectroscopic properties of the new derivatives were used to compare the electronic effects produced on the complexes by varying the coordinated phosphine. As convenient tools were chosen the ³¹P NMR and ¹³C NMR chemical shifts because the C-O stretching frequency in the IR spectra is not a good indicator of the phosphine donor strength in these compounds.³¹ The NMR data for **3b** are not much different from those of **3a** (see Table 3), which indicates only minor modification of the electronic properties of the metal-complex upon formal addition of the trimethylsilyl groups. The NMR data of 3a slightly differ from those corresponding to the cobalt complex with the tertbutyl-substituted arylphosphine 3d, which reflects the expected electron-donating effect of the alkyl groups. In fact, despite the inductive effect of the Me₃Si group, it appears to be only a modest electron donor, poorer than the alkyl groups. This phenomenon can be attributed to an electron-withdrawing component in the behaviour of the silicon, in which charge from the aromatic ring is delocalized through backdonation into the antibonding orbitals of the SiC_3 framework, cancelling the electron-donating effect of the methyl groups in the TMS group.³²

Similar tendencies are maintained in the CpCoI₂L series. These derivatives are easily obtained by reaction of CpCoI₂(CO) with the corresponding arylphosphine, following the same procedure described for the synthesis of the PPh₃ derivative 4a.²⁰ The ³¹P NMR data of the diiodo derivatives revealed the same trend observed above for the series of cobalt carbonyl complexes (see Table 3). The chemical shifts for 4b and 4c are close to that of 4a (maximum change of 0.3 ppm), while those of 4d and 4e are shifted by 3.4 and 1 ppm, respectively. These facts confirm again the small effect created by the TMS groups on arylphosphine properties.

The series of *trans*-[PdCl₂L₂] ($L = P(4-Me_3SiC_6H_4)_3$ **5b**, P(C₆H₅)₂(4-Me₃SiC₆H₄), **5c**) complexes were prepared by the reaction of PdCl₂ with two equivalents of the arylphosphine ligand. The already known 4-H (**5a**)²¹ and 4-CF₃ (**5e**)²² substituted triarylphosphine palladium complexes were also prepared in order to compare their spectroscopic properties with the TMS derivatives. The Pd–Cl stretching frequency of the palladium series was not too sensitive to the electronic influence of the 4-substituted groups (see Table 4).

Compound	ν (M–Cl)/cm ⁻¹	$\delta(^{31}\text{P})^a/\text{ppm}$
$PdCl_2[P(C_6H_5)_3]_2$ (5a)	358 (360) ^b	22.2
$PdCl_{2}[P(4-Me_{3}SiC_{6}H_{4})_{3}]_{2}$ (5b)	360	22.7
$PdCl_{2}[P(C_{6}H_{5})_{2}(4-Me_{3}SiC_{6}H_{4})]_{2}$ (5c)	362	22.6
$PdCl_{2}[P(4-F_{3}CC_{6}H_{4})_{3}]_{2}$ (5e)	364	23.9 ^c
"Solvent CDCL bData taken from ref	1 Data takan from	ref 22

Solvent, CDCl₃. ^bData taken from ref. 21. ^cData taken from ref. 22.

Table 5 Solubility of cobalt complexes in $scCO_2$ at 40 °C and different pressures

$CpCo(CO)[P(C_6H_5)_3]$ (3a)		CpCo(CO)[P(4-Me ₃ SiC ₆ H ₄)]	3] (3b)
Solubility (g ml ⁻¹ 10 ⁴ CO ₂)	P/bar	Solubility (g ml ⁻¹ 10 ⁴ CO ₂)	P/bar
1.59	160	5.95	166
1.83	178	6.21	188
1.88	188	6.1	204
1.99	205		

However, the ³¹P NMR chemical shifts show the same trend previously observed for the arylphosphines.

Solubility of triarylphosphine-complexes in scCO₂

The newly synthesised TMS-substituted cobalt complex **3b** was used to study the solubilising effects of the TMS groups in $scCO_2$. For comparison, the measurements were performed in parallel to that of the well-known non-substituted derivative **3a**. It should be noted that complexes **4** and **5** are not soluble in $scCO_2$, so it was not possible to evaluate the effect that the presence of TMS groups have in the solubility properties of these complexes. Solubility measurements in $scCO_2$ were carried out by taking samples through a high-pressure sample loop followed by UV spectroscopy analysis, as described elsewhere.¹¹ As summarised in Table 5, the concentration of **3b** in $scCO_2$ was estimated to be more than three times higher than that of **3a** (see graph in ESI[†]).

Enhancement of the solubility of the arylphosphine cobalt complex in $scCO_2$ upon formal substitution with Me₃Si groups is low, but it is interesting to emphasize that these solubilisers do not interfere with the chemical properties of the coordinated metal centre. This idea could be used in the design of new catalysts soluble in $scCO_2$ just by adding Me₃Si groups to the metal complexes used in conventional homogeneous catalysis. The resulting systems should be more soluble in the supercritical media while maintaining their catalytic activities. This approach has been recently adopted in the rhodium-catalysed hydroformylation of olefins in $scCO_2$.¹³

Conclusion

The Me₃Si groups, introduced as substituents in triarylphosphines, can enhance the solubility of metal complexes in scCO₂ without greatly affecting the electronic properties of the metal centre. These observations agree with our previous work on transition metal catalysts with TMS-substituted cyclopentadienyl ligand. Nevertheless, the increase in the solubility of the metal complexes

in scCO₂ using either TMS-substituted triarylphosphine or cyclopentadienyl ligands is quite modest to be used as a systematic solution in order to solubilise metal-complexes in the supercritical medium. New approaches have to be made in order to design new scCO₂ homogeneously catalysed processes based on traditional catalytic systems. With respect to this, we are presently attempting to increase the solubility of selected catalysts in scCO₂ by introducing polysiloxane chains pendant to the ligands.

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