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Preparation and NMR studies of cobalt-containing diphosphine ligand chelated W, Ru, Au and Pd complexes: Suzuki cross-coupling reactions and carbonylation catalyzed by the Pd complex

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Treatment of a cobalt-containing diphosphine ligand, $[{\mu-P,P-PPh_2CH_2PPh_2}Co_2(CO)_4{\mu-PPh_2C=CPPh_2}]$ **1** with metal complexes W(CO)₆, Ru₃(CO)₁₂, AuCl(tht) (tht = tetrahydrothiophene) and (COD)PdCl₂ (COD = 1,5-cycloctadiene) gave 1-chelated metal complexes $[(1)W(CO)_4]$ **3**, $[(\mu-1)Ru_3(CO)_{10}]$ **4**, $[(1)(AuCl)_2]$ **5** and $[(1)PdCl_2]$ **6**, respectively. All these compounds were characterized by spectroscopic means whereas **3**, **4** and **6** were also studied by X-ray diffraction. These compounds display chelating and bridging modes of metal–phosphine complexation. Variable-temperature ¹H and ³¹P NMR experiments were carried out for **3–6** and revealed that the fluxional behavior of each individual bridging dppm fragment was affected greatly by the bite angle of **1** in each metal complex. Suzuki cross-coupling reactions were satisfactorily catalyzed by **6** under mild conditions. The reactions of aryl halides or iodothiophenes with chloroform and alkali in biphasic solution utilizing a catalytic amount of **6** result into the formation of benzoic and thiophenic acids, respectively.

1 Introduction

The applications of bidentate phosphine ligands in transition metal-based homogeneous catalysis are well known.¹ Nevertheless, reports on the preparations of the metal-containing bidentate phosphine ligands are rare.² Previously we have described the preparation of a new type of metal-containing bidentate $[(\mu-Ph_2PCH_2PPh_2)Co_2(CO)_4(\mu-PPh_2C=$ phosphine ligand CPPh₂)] 1, which was obtained from the reaction of a bifunctional ligand bis(diphenylphosphino)acetylene (dppa) with one equivalent of a bis(diphenylphosphino)methylene (dppm) bridged dicobalt complex Co₂(CO)₆(µ-Ph₂PCH₂PPh₂).³ Interestingly, methylene peaks of 1 do not appear in the ¹H NMR spectrum at room temperature but do appear at temperatures below 10 °C when a variable-temperature ¹H NMR experiment was carried out. This indicates that the coordinated dppm inhibits fluxional behavior and the coalescence temperature for the thermal motion happens to be close to room temperature thus causing the disappearance of the methylene peaks in the ¹H NMR spectrum.

The chelating and bridging capability of **1** as a bidentate phosphine ligand toward metal complexes was demonstrated elsewhere.^{3,4} The reaction of **1** with $Mo(CO)_6$ resulted in the formation of $[(1)Mo(CO)_4]$ **2** in satisfactory yield (Scheme 1). In contrast to the case of free ligand **1**, one set of triplet signals is observed for the methylene protons of dppm for **2** in the ¹H NMR spectrum at room temperature. A variable-temperature experiment was carried out for **2** and the coalescence temperature appears around -50 °C. An explanation for this difference is explored here.

We report herein some notable results of **1** as a ligand in the formation of tungsten, ruthenium, gold and palladium metal complexes. The fluxional behavior of the bridging dppm ligand in these complexes are described from variable-temperature NMR studies and compared.

Palladium-catalyzed Suzuki cross coupling reactions⁵ have received much interest in various disciplines of chemistry⁶ owing to its ability to create sp²–sp² carbon–carbon bonds. A significant expansion in the scope of the Suzuki crosscoupling reactions was achieved recently by Fu and co-workers in which coupling occurred under mild conditions for some relatively inactivate alkyl bromides, those containing β -hydrogens, with various phenylboronic acids.⁷ Meanwhile, the catalytic carbonylation of haloarenes in biphasic solution with phosphine-modified palladium complexes has been extensively studied.⁸ Different strategies have been pursued to improve the efficiency of the reductive elimination step during the catalytic cycle. One of the approaches is using Pd complexes containing bulky chelating diphosphines.⁹

To display the catalytic capacity of **6** in this work, we further report one more successful example of the cross-coupling reaction using benzyl bromide as the halide source. In addition, some interesting results from the catalytic reactions of a **1**-chelated palladium complex in Suzuki cross-coupling reactions as well as carbonylation reactions performed in a water/ organic biphasic system are reported.

2 Results and discussion

2.1 Reactions of 1 with tungsten, ruthenium, gold and palladium metal complexes

Treatment of 1 with the metal complexes W(CO)₆, Ru₃(CO)₁₂, AuCl(tht) (tht = tetrahydrothiophene) and (COD)PdCl₂ (COD 1,5-cyclooctadiene) gave the 1-chelated metal complexes [(1)W(CO)₄] 3, [(µ-1)Ru₃(CO)₁₀] 4, [(1)(AuCl)₂] 5 and [(1)PdCl₂] 6, respectively (Scheme 1).¹⁰ All these compounds were characterized by spectroscopic means. Similar to the case of [(1)Mo- $(CO)_4$ 2, triplet signals at 3.24, 3.16 and 3.83 ppm were observed in the ¹H NMR spctra for the corresponding methylene protons of dppm in 3, 4 and 5, respectively; in the case of 6 this signal appears at 2.98 ppm. These results indicate that the thermal motion of the bridged dppm fragment in all compounds are relatively fast at ambient temperature, thus causing the two methylene protons to be magnetically equivalent.³ In the ³¹P NMR spectra broad signals at 35.4, 37.7, and 37.3 ppm were observed for the corresponding chelated phosphorus atoms of dppa in 3, 4 and 5, respectively; in the case of 6 this signal appears at 48.9 ppm. A much larger downfield shift to the palladium-coordinated phosphorus atom implies that more electron density has been donated to the Pd(II) metal center. A triplet corresponding to the methylene carbon of the dppm

Table 1Crystal data for 3, 4 and 6

Compound	3	4	6
 Formula	C ₅₉ H ₄₂ Co ₂ O ₈ P ₄ W·CH ₂ Cl ₂ ·C ₄ H ₈ O	C ₆₅ H ₄₂ Co ₂ O ₁₄ P ₄ Ru ₃	C ₅₅ H ₄₂ Cl ₂ Co ₂ O ₄ P ₄ Pd·CH ₂ Cl ₂
Formula weight	1461.55	1591.94	1270.85
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P\overline{1}$	$P2_1/n$
aĺÅ	11.728(8)	11.5252(10)	11.4509(5)
b/Å	23.473(16)	14.3431(12)	19.4456(8)
c/Å	21.969(15)	20.8540(17)	24.4529(10)
a/°	_	75.587(2)	_
βl°	90.465(13)	83.309(2)	96.0140(10)
y/°	_	71.361(2)	_
V/Å ³	6048(7)	3161.1(5)	5415.0(4)
Ζ	4	2	4
$D_{\rm c}/{\rm Mg}~{\rm m}^{-3}$	1.605	1.672	1.559
λ (Mo-Ka)/Å	0.71073	0.71073	0.71073
μ/mm^{-1}	2.690	1.380	1.295
2θ Range/°	1.85-26.20	1.64-26.03	1.34-26.00
Observed reflections $(F > 4\sigma(F))$	5841	4251	6238
No. of refined parameters	710	793	640
<i>R</i> 1 ^{<i>a</i>} for significant refletns	0.0647	0.0456	0.0416
$wR2^{b}$ for significant reflectns	0.1344	0.1040	0.0852
'GoF	1.110	0.821	0.974

^{*a*} $R1 = |\Sigma(|F_o| - |F_c|)/|\Sigma|F_o||$. ^{*b*} $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2/\Sigma[w(F_o^2)^2]\}^{1/2}$; w = 0.0391, 0.0727, 0.045 for **3**, **4** and **6**. ^{*c*} GoF = $[\Sigma w(F_o^2 - F_c^2)^2/(N_{rfins} - N_{params})]^{1/2}$.



Scheme 1

fragment was observed in the ¹³C NMR for **6**. Unfortunately, the carbon signals for carbonyls and two acetylenic carbons could not be observed even after long acquisition time.

Suitable crystals of **3**, **4** and **6** were obtained from CH_2Cl_2 hexane (1 : 1) at 4 °C and their structures were determined by X-ray diffraction (Tables 1 and 2). The crystal structures reveal that the main skeletons of **2** and **3** are almost identical (Fig. 1). The structure of **3** could be viewed as a W(CO)₄ fragment being chelated by **1**. Here, the bidentate phosphine ligand **1** can be regarded as a metal-containing version of 1,2-bis(diphenylphosphino)ethane (dppe), a widely used bidentate phosphine ligand.¹¹ The structure of **4** (Fig. 2) shows that the bidentate phosphine acts as a bridging ligand and adopts the equtorial position of the triruthenium cluster, which is in accordance with common observations for disubstituted triruthenium clusters.¹² The distance between the two bridging phosphorus atoms in **4** is 3.944 Å, a little longer than the 3.893 Å found for a dppe bridged triruthenium cluster $[(\mu-P, P-Ph_2PCH_2CH_2-PPh_2)Ru_3(CO)_{10}]$.¹³ The structure of **6** can be viewed as a PdCl₂ fragment being chelated by **1** and is a typical square-planar Pd(II) complex with a d⁸ configuration. Crystal data reveal that the bond angles for P(2)–Pd–P(1), P(2)–Pd–Cl(2), P(1)–Pd–

Table 2	Comparison	of selected structural	parameters	of 3, 4 and 6
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	3	4	6
Bond lengths/Å			
Co(1)–Co(2)	2.477(2)	2.4724(11)	2.5074(8)
C(1)-C(2)	1.352(10)	1.361(7)	1.370(6)
C(1)–Co(1)	1.992(7)	2.000(5)	1.962(4)
C(1)–Co(2)	1.995(9)	2.014(6)	1.971(4)
C(2)–Co(1)	1.974(7)	1.969(5)	1.950(4)
C(2) - Co(2)	1.920(9)	1.983(6)	1.960(4)
C(1) - P(1)	1.841(8)	1.819(6)	1.813(4)
C(2) - P(2)	1.818(8)	1.824(6)	1.798(4)
Co(1) - P(3)	2.230(3)	2.2428(17)	2.2522(14)
Co(2) - P(4)	2.245(3)	2.2694(17)	2.2427(13)
C(55)-P(3)	1.826(9)	1.825(5)	1.830(4)
C(55) - P(4)	1.837(9)	1.827(5)	1.828(4)
P(1)–M	2.564(2)	2.3603(15)	2.2611(12)
P(2)–M	2.509(3)	2.3599(17)	2.2608(12)
Bite distances/Å			
$\overline{\mathbf{P}(1)\cdots\mathbf{P}(2)}$	3.252	3.944	3.101
Angles/°			
P(1)-C(1)-C(2)	155.1(4)	131.9(4)	115.8(3)
P(2)-C(2)-C(1)	123.9(6)	138.5(4)	121.4(3)
Co(1)-C(1)-Co(2)	76.8(3)	76.1(2)	79.22(15)
Co(1)-C(2)-Co(2)	79.0(3)	77.4(2)	79.78(16)
C(1)-Co(1)-C(2)	40.2(3)	40.1(2)	40.99(16)
C(1)-Co(2)-C(2)	39.9(3)	39.8(2)	40,79(16)
P(3)-C(55)-P(4)	107.8(4)	110.7(3)	113.0(2)
$C_0(1) - P(3) - C(55)$	108.9(3)	110.10(18)	108.55(15)
$C_0(2) - P(4) - C(55)$	107.2(3)	108.25(19)	107.75(15)
$P(3) = C_0(1) = C_0(2)$	91 25(9)	91.83(5)	97 21(4)
	2 		~



Fig. 1 The molecular structure of 3. Hydrogen atoms are omitted for clarity.

Cl(1) and Cl(2)–Pd–Cl(1) are 86.60(4), 89.53(5), 90.18(5) and 93.70(5)°, respectively. The bond lengths of Pd–Cl(2) and Pd–Cl(1) are 2.3556(13) and 2.3579(12) Å, respectively, while the bond lengths of Pd–P(1) and Pd–P(2) are 2.2611(12) and 2.2608(12) Å, respectively. They are within the common observed bond lengths for Pd(π)–Cl or Pd(π)–P bonds. We found here that the bite angle P(2)–Pd–P(1) in **6** (Fig. 3) was



Fig. 2 The molecular structure of 4. Hydrogen atoms are omitted for clarity.



Fig. 3 The molecular structure of 6. Some atoms are omitted for clarity.

slightly larger than that of a closely related compound (μ_2 -*P*,*P*-PPh₂CH₂CH₂PPh₂)PdCl₂.¹⁴ The bite distance between P(1) and P(2) is 3.101 Å, which falls within the normal range of 1-chelated complexes. Unfortunately, attempts to grow suitable crystals of **5** for X-ray studies were not successful. Judging from the collected spectroscopic data, the main structure of **5** was tentatively assigned as shown in Scheme 1. Two AuCl fragments were coordinated each by two phosphorus sites of **1**. There is also a possibility for the presence of a metal–metal bond between two gold atoms.¹⁵

The bite angle (θ) and the bite distance (r) between the two phosphorus atoms of a bidentate phosphine ligand complexed metal complex are two vital factors for its catalytic efficiency.¹⁶ The bite angles are 79.60(2), 79.76(8) and 86.60(4)°, respect-



Fig. 4 Variable-temperature ³¹P and ¹H NMR spectra of 3 in CD₂Cl₂.



Fig. 5 Variable-temperature ³¹P and ¹H NMR spectra of 4 in CD₂Cl₂.

ively, for metal complexes **2**, **3** and **6**, while the bite distances are 3.275, 3.252 and 3.101 Å, respectively. Among these compounds, **6** has the shortest bite distance and the largest bite angle.



2.2 Variable-temperature NMR experiments for 2–6

Variable-temperature ¹H NMR experiments were carried out for **3–6** in CD₂Cl₂ over the range of -90 to 20 °C (Figs. 4–7). Measurements were taken at intervals of 5 or 10 °C. The coalescence temperatures for dppm in free ligand 1 as well as metal complexes 2-6 are *ca*. 40, -50, -60, -10, -20 and -10 °C, respectively. The methylene peaks split into two sets of multiplet signals below that temperature. It was found that the coalescence temperatures for 2 and 3 were almost identical, which was in agreement with their striking similarity in structures. The coalescence temperatures of 4, 5 and 6 are much higher than in cases of 2 and 3.

Variable-temperature ³¹P NMR experiments were also carried out for 3–5. The shapes and locations of peaks were slightly shifted with variation of temperature. The coalescence temperatures for the dppm methylene protons in metal complexes 3, 4 and 5 are at *ca.* –65, 0 and 10 °C, respectively. This trend is in accord with the ¹H NMR experiments.

Some selected spectroscopic data and the activation energies of the fluxional dppm of several 1-related complexes are shown in Table 3 for comparison. The activation energies of the dppm fluxional motion are lower for metal complexes than for ligand 1 indicating that the thermal motions of the dppm fragments were much easier in the metal complexes than in the free ligand. As it was revealed from the crystal structures, the chelation of 1 towards a metal center causes the two phosphorus atoms of the dppa fragment to bend towards the metal center(s). The



Fig. 6 Variable-temperature ³¹P and ¹H NMR spectra of 5 in CD₂Cl₂.



Fig. 7 Variable-temperature 1 H NMR spectra of 6 in CD₂Cl₂. Asterisked peaks are from an impurity.

narrower the bite angle (*a*), the closer the phenyl rings (of dppa) to the metal center. Therefore, the steric hindrance between phenyl rings of dppa and of dppm will be more relaxed and

 Table 3
 ¹H NMR of methylene protons with activation energies of the fluxional dppm and ³¹P NMR of the corresponding dppa of 1-related complexes

	¹ H NMR (δ/ppm) ^a	$\Delta E_{\rm a}/{\rm kcal}~{\rm mol}^{-1}$	³¹ P NMR $(\delta/\text{ppm})^b$
1	_	19.2	-14.7, 1.2
2	3.21	7.1	33.9
3	3.24	9.2	35.4
4	3.16	19.7	37.7
5	3.83	28.9	37.3
6	2.98	14.1	48.9
<i>a</i> –C	$^{2}H_{2}$ of dppm; ^b P atoms	of dppa.	

allow the dppm fragment to have more room to wag back and forth. Thus it will become more difficult to freeze the fluxional behavior of dppm in the metal complexes. This also explains the increased fluxionality of 2 and 3 relative to that of 4, 5 and 6. A sterically hindered model is proposed for 1-chelated metal complexes to account for the fluxional behavior of the bridging dppm ligand (Fig. 8).

2.3 Catalytic Suzuki coupling reactions by 6

Suzuki and co-workers nicely demonstrated a series of crosscoupling reactions of B-alkyl-9-borabicyclo[3,3,1]nonanes (B-R-9-BBN) with 1-halo-1-alkenes (or haloarenes) in water/ organic mixed media¹⁷ by utilizing $[PdCl_2(dppf)]$ (dppf = 1,1'bis(diphenylphosphino)ferrocene), a structural analogue of 6 reported by Hayashi et al.,18 as a working catalyst. In the light of their work, we therefore employed 6 as the operational catalyst in Suzuki type cross-coupling reactions and obtained satisfactory results as shown in Table 4. The coupling reactions for phenylboronic acid and bromohalides were carried out in the presence of a catalytic amount of 6 (1 mol%). Complex 6can be regarded as a bulky diphosphine chelating palladium compound, where the diphophine is comprised by of a dicobalt-containing organometallic moiety. The catalytic reactions were carried out at 65 °C for 16 h in a biphasic solvent (THF/H₂O). 3 M NaOH was employed in the biphasic medium whilst 2.2 molar equivalents of K₃PO₄ was added for

Table 4	Biphasic Suzuk	i-coupling reaction	of halides by 6
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- Diplusic Suzuki coupling reaction of numers by 0						
	Entry	Halide	Solvent	Temp./ °C	Time/h	Isolated yield (%)
	1 <i>a</i>	∕_Br	THF/H ₂ O (5 : 1)	65	16	>99
	2 <i>ª</i>	S →Br	THF/H ₂ O (5 : 1)	65	16	88.4
	3 <i>ª</i>	HO-	THF/H ₂ O (5 : 1)	65	16	97.7
	4 <i>ª</i>	O HC→Br	THF/H ₂ O (5 : 1)	65	16	71.6
	5 <i>ª</i>	∭Br	THF/H ₂ O (5 : 1)	65	16	67.8
	6 <i>ª</i>	Br	THF/H ₂ O (5 : 1)	65	16	87.2
	7 ^b		Toluene	65		88.0
	8 <i>a</i>	Br	THF/H ₂ O (5 : 1)	65	16	69.8
	9 ^{<i>b</i>}	·	Toluene	65	16	90.0

^{*a*} Reactions were conducted in a biphasic solvent (THF/H₂O) at 65 °C with 1.0 equiv. aryl bromide, 1.5 equiv. phenylboronic acid, 3.0 equiv. NaOH(aq) and 1 mol% of 6. ^{*b*} Reactions were conducted in toluene at 65 °C with 1.0 equiv. aryl bromide, 1.5 equiv. phenylboronic acid, 2.2 equiv. K₃PO₄ and 1 mol% of 6.



Fig. 8 Proposed steric hindrance model for 1-chelated metal complexes. Some atoms are omitted for clarity.

experiments in toluene. Almost quantitative yield (>99%) was obtained when bromobenzene is used as the halide source (entry 1). The reaction was not efficient (88.4%) when the less reactive 2-bromothiophene was used (entry 2). A stronger C_{ipso} -Br bond in 2-bromothiophene than that of bromobenzene could be the reason for the decrease in catalytic efficiency of the former compound. 4-Bromophenol, having a π electrondonating group at the *para*-position gave a rather high yield, i.e. 97.7% of the coupling product (entry 3). A significant drop in yield, 71.6% (entry 4), was observed using 4-bromobenzaldehyde as the halide source and the reason for this was not clearly understood. As demonstrated in entry 5 the steric effect of an ortho-substituted substrate resulted in a lower yield, 67.8%, when using 2-bromotoluene as the halide source. By contrast, a higher yield, 87.2%, was obtained for reaction carried out from a para-substituted substrate, 4-bromotoluene (entry 6). The yields are about the same when the reaction solvent system was changed from the biphasic medium to toluene (entry 7). Significantly, a fairly high yield, 90%, was obtained employing benzyl bromide as the halide source when the coupling reaction was carried out in toluene under mild conditions (entry 9). Contrarily, the yield, 69.8%, is not as good in the biphasic system (entry 8). This encouraging result urges us to invest more effort on sp^2-sp^2 cross-coupling processes employing complex 6 as the operational catalyst. An extensive examination is currently under way.

2.4 Catalytic carbonylation of organic halides by 6

The catalytic potentials of various phosphine coordinated palladium complexes toward the process of carbonylation of organic halides with chloroform and alkali in biphasic solution were investigated. The carbonyl is believed to be generated from the reaction of chloroform with alkali, usually NaOH.19 To the best of our knowledge, carbonylation catalyzed by a palladium complex with such a bulky diphosphine chelate such as 6 has not been attempted previously. The reactions of aryl halides with chloroform and alkali in the presence of a catalytic amount of 6 (5 mol%) resulted in the formation of benzoic acid (Scheme 2). Poor yields are obtained in the case of bromo- or chlorobenzene when compared to iodobenzene as reagent (Table 5). For comparison, the same experimental procedures were carried out for iodobenzene and chloroform and alkali with only free ligand, 1, with no benzoic acid found to form. It is safe to state that the cobalt centers of the free ligand, 1, do not interfere in the catalytic process of the carbonylation.



Similar procedures were employed for 6-catalyzed carbonylation of various substituted iodoarenes with chloroform. As

Table 5 Biphasic carbonylation of phenyl halides with chloroformcatalyzed by 6^a

Entry	х	Isolated yield (%)
1	I	42.4
2	Br	ND ^b
3	Cl	ND

 a 1.5 mmol of phenyl halide, 5 g of 60% KOH, 1 ml of CHCl_3, 0.075 mmol of 6, N_2, 25 °C, 24 h. b Not-detected.

Table 6 Biphasic carbonylation of iodoarenes with chloroform catalyzed by 6^a

Entry	Ar	Isolated yield (%)
1	C ₆ H ₅	42.2
2	2-CH ₃ C ₆ H ₄	2.7
3	3-CH ₃ C ₆ H ₄	2.9
4	4-CH ₃ C ₆ H ₄	2.9

 a 1.5 mmol of aryl halide, 5 g of 60% KOH, 1 ml of CHCl_3, 0.075 mmol of 6, N_2, 25 °C, 24 h.

Table 7 Biphasic carbonylation of thiophene halides with chloroformcatalyzed by 6^a

Entry	Substituent	Isolated yield (%)
1 2 3	CH3 I	37.9 1.3 _ ^b

 a 1.5 mmol of thiophene halides, 5 g of 60% KOH, 1 ml of CHCl₃, 0.075 mmol of 6, N₂, 25 °C, 24 h. b Mixed products.

shown in Table 6, rather poor yields were obtained when substituted iodobenzenes were used as reactants.

Following a similar reaction procedure, thiophenic acid was observed as the product from the catalyzed carbonylation of thiophenes with chloroform in the presence of a catalytic amount of 6 (5 mol%). (Scheme 3). Unsubstituted iodothiophene led to a good yield compared to substituted iodothiophenes and the results are depicted in Table 7.

(X)
$$(X) \xrightarrow{S} I + CHCl_3 \xrightarrow{1.6, OH^-} (X) \xrightarrow{S} C \xrightarrow{O} OH^-$$

Scheme 3

Preliminary results show that the bulky diphosphine ligandchelated palladium complex $\mathbf{6}$ acts as a catalyst in the carbonylation of organic halides in the presence of chloroform and alkali. The retardation of the carbonylation by $\mathbf{6}$ might be accounted by a strong bonding between the diphosphine ligand $\mathbf{1}$ with palladium as well as the bulkiness of the ligand. More detailed investigations of these reactions are currently under progress.

3 Summary

In this work, several 1-chelated metal complexes were prepared and the fluxional behaviors of the bridging dppm on complexes were examined by variable-temperature NMR experiments. The results show the steric hindrances between phenyl rings of the complexes strongly affect the thermal motion of the dppm in the complexes. The bite angle for the metal complex is the predominant factor determining the degree of steric hindrance. We also described the catalytic carbonylation toward organic halides and the Suzuki cross-coupling reactions in the presence of catalytic amounts of $\bf{6}$. The former reaction showed satisfactory results, while the latter, in some cases, showed quantitative yields.

4 Experimental

4.1 General

All operations were performed in a nitrogen flushed glove box or in a vacuum system using freshly distilled solvents. Separations of the products were performed by Centrifugal Thin Layer Chromatography (CTLC, Chromatotron, Harrison model 8924). ¹H NMR spectra were recorded (Varian VXR-300S spectrometer) at 300.00 MHz and chemical shifts were reported in ppm relative to internal CHCl₃ or CH₂Cl₂. ³¹P and ¹³C NMR spectra were recorded at 121.44 and 75.46 MHz, respectively. ¹H NMR spectra of variable temperature experiments were recorded on the same instrument. Routine ¹H NMR spectra were recorded on a Gemini-200 spectrometer at 200.00 MHz or Varian-400 spectrometer at 400.00 MHz. IR spectra of sample powders in KBr were recorded on a Hitachi 270-30 spectrometer. Mass spectra were recorded on a JOEL JMS-SX/ SX 102A GC/MS/MS spectrometer. Elemental analyses were recorded on a Heraeus CHN-O-S-Rapid instrument. Accurate elemental analyses were precluded for the following compounds probably due to their chemical lability.

4.1.1 Preparation of 3. Complex 1 (0.178 g, 0.176 mmol) and two molar equivalents of $W(CO)_6$ (0.124 g, 0.356 mmol) with 5 cm³ of toluene were taken in a 100 cm³ flask. The solution was refluxed for 15 h and the mixture was filtered through a small amount of silica gel. Purification was carried out by using centrifugal thin-layer chromatography (CTLC). The first dark brownish band 3 (0.148 g, 0.113 mmol), was eluted using CH₂Cl₂-hexane (1 : 1): yield 64.3%.

Dark brownish solid; ¹H NMR (CD₂Cl₂, δ /ppm): 7.05–7.74 (m, 40H, arene), 3.24 (t, $J_{P-H} = 10.8$ Hz, CH₂ of dppm); ¹³C NMR (CD₂Cl₂, δ /ppm): 209.13 (1CO of W), 205.21 (1CO of W), 203.53 (2CO of W), 128.24–139.14 (48C, arene); ³¹P NMR (CD₂Cl₂, δ /ppm): 32.8 (2P of dppm), 35.4 (2P of dppa); IR (CH₂Cl₂) ν (CO): 2039 (m), 2011(s), 1983(m) cm⁻¹; Anal. Calc. for **3**: C, 55.45; H, 3.99. Found: C, 52.40; H, 3.75%; MS (FAB): *m*/z 1305 (M⁺).

4.1.2 Preparation of 4. The same procedure as described for **3** was followed. Complex **1** (0.3812 g, 0.3779 mmol) with one molar equivalent of $\text{Ru}_3(\text{CO})_{12}$ (0.2416 g, 0.3779 mmol) and 10 cm³ of toluene were placed in a 100 cm³ flask. The solution was stirred at 60 °C for 6 h. The first red–orange band **4** (0.2595 g, 0.1630 mmol) was eluted using CH₂Cl₂–hexane (1:1): yield 43.1%.

Red-orange solid; ¹H NMR (CDCl₃, δ /ppm): 6.98–7.76 (m, 40H, arene), 3.16 (t, CH₂ of dppm); ¹³C NMR (CDCl₃, δ /ppm): 211.70 (CO of Ru), 198.99 (CO of Ru), 127.68–139.93 (48C, arene); ³¹P NMR (CDCl₃, δ /ppm): 22.6 (2P of dppm), 37.7 (2P of dppa); IR (CH₂Cl₂) v(CO): 2077 (m), 2005 (s), 1965 (m) cm⁻¹; Anal. Calc. for **4**: C, 49.43; H, 3.34. Found: C, 50.63; H, 6.17%; MS (FAB): *m*/*z* 1591.93 (M⁺ – 3CO).

4.1.3 Preparation of 5. The gold compound [AuCl(tht)] (tht = tetrahydrothiophene) was prepared according to the literature.²⁰ Compound **1** (0.565 g, 0.560 mmol) with two molar equivalents of AuCl(tht) (0.359 g, 1.119 mmol) and 10 cm³ of CH₂Cl₂ were placed into a 100 cm³ flask. The solution was stirred at 25 °C for 1 h. The first pink-red band **5** (0.629 g, 0.427 mmol) was eluted using CH₂Cl₂: 76.3%.

Pink-red solid; ¹H NMR (CD₂Cl₂, δ /ppm): 7.25–7.69 (m, 40H, arene), 3.83 (t, CH₂ of dppm); ¹³C NMR (CD₂Cl₂, δ /ppm): 128.78–135.38 (48C, arene); ³¹P NMR (CD₂Cl₂, δ /ppm): 30.8 (2P of dppm), 37.3 (2P of dppa); IR (CH₂Cl₂) ν (CO): 2038 (m), 2012 (s), 1983 (m) cm⁻¹; Anal. Calc. for **5**: C, 44.83; H, 2.87. Found: C, 44.21; H, 3.25%; MS (FAB): *m*/*z* 1473.54 (M⁺).

4.1.4 Preparation of 6. The same procedure described for 3 is followed for the preparation of 6. Complex 1 (0.349 g, 0.346 mmol) and dichloro(1,5-cyclooctadiene)palladium (0.099 g, 0.346 mmol) with 20 cm³ of THF were taken in a 100 cm³ round flask. The solution was frozen and degassed followed by filling up with purified nitrogen. Then it was allowed to warm up to 25 °C and stirred for 2 h. Subsequently the resulting yellowish brown solution was filtered through silica gel and purification with centrifugal thin-layer chromatography (CTLC) was carried out. The first pink band of the known compound $[\{\mu-P, P-PPh_2CH_2PPh_2\}Co_2(CO)_4\{\mu-P(=O)Ph_2C\equiv CP(=O)Ph_2\}],$ was eluted with CH₂Cl₂. The second yellow band of 6 was eluted with CH₂Cl₂-MeOH (10:1). The solvent was removed in vacuo and was identified as 6; 55% yield (0.225 g, 0.189 mmol). Compound 6 can be obtained by an alternative route as described below. Pd(OAc)₂ (0.082 g, 0.367 mmol) and one equivalent of 1 (0.371 g, 0.367 mmol) were dissolved in 20 cm³ of methanol and THF, respectively, in a 100 cm³ flask. The solution was stirred at 25 °C for 45 min. Subsequently, 1 equivalent of dry CoCl₂ (0.080 g, 0.367 mmol) was added to the solution under nitrogen and stirred at 25 °C for 2 h. The similar separation procedure as above is followed for obtaining 6 and the isolated yield is 50% (0.218 g, 0.184 mmol).

Yellow solid; ¹H NMR (CD₂Cl₂, δ /ppm): 2.98 (t, 2H, CH₂), 6.98–7.94 (m, 40H, arene); ¹³C NMR (CDCl₃ δ /ppm): 36.13 (t, 1C, CH₂), 128.65 (d, 8C, arene); ³¹P NMR (CD₂Cl₂ δ /ppm): 35.9 (2P of dppm), 48.9 (2P of dppa); IR (KBr): *v*(CO) 2101, 2927 cm⁻¹; Anal. Calc. for **6**: C, 55.7; H, 3.57. Found: C, 54.52; H, 3.81%; MS (FAB): *m*/*z* 1151 (M⁺ – Cl); mp = 162–180 °C (decomp.).

4.2 General procedures for the Suzuki cross-coupling reactions

Suzuki cross-coupling reactions were performed according to the following procedures.

Method a^{21} (conducted in a THF-H₂O biphasic medium). Complex 6 (0.012 mg, 0.010 mmol) and phenylboronic acid (0.183 g, 1.500 mmol) were charged into a suitable oven-dried Schlenk flask. The flask was evacuated and backfilled with nitrogen before adding THF (5 mL), 3 M NaOH solution (1 mL) and aryl halide (1.000 mmol). Note that solid aryl halides were added prior to the evacuation/backfill cycle. The flask was sealed with a Teflon screw cap and the solution was stirred at 65 °C for 16 h. The mixed solution was extracted with toluene (20 mL), dried with anhydrous magnesium sulfate, filtered and concentrated *in vacuo*. The crude material was purified by flash chromatography on silica gel.

Method b (conducted in a toluene medium). Complex 6 (0.012 mg, 0.010 mmol), the phenylboronic acid (0.183 g, 1.500 mmol) and K_3PO_4 (0.425 g, 2.000 mmol) were charged into a suitable oven-dried Schlenk flask. The flask was evacuated and backfilled with nitrogen before adding toluene (1 mL) and the aryl halide (1.000 mmol) through a rubber septum. The mixture was washed with aqueous NaOH (1 M, 20 mL) and the aqueous layer was extracted with ether (20 mL). The combined organic layer was washed with brine (20 mL) and dried with anhydrous magnesium sulfate, filtered, and concentrated *in vacuo*. The crude material was purified by flash chromatography on silica gel.

4.3 General procedures for the catalytic carbonylation reactions

1.5 mmol of aryl halide, 5 g of 60% KOH and 1 cm³ of CHCl₃ were taken in a 100 cm³ round flask. and. The solution was frozen and degassed, followed by filling up with purified nitrogen. Then, 0.075 mmol of **2** was added and the solution was stirred at 25 °C for 24 h. The solution was then placed into a separator funnel followed by adding 30 cm³ of degassed water

and 20 cm³ of ether. Then, the water layer was extracted and acidified with 20% HCl. After extraction again with ether (3×30 cm³) the organic phase was collected and dried with anhydrous MgSO₄. The product was collected and measured after filtration and concentration.

4.4 X-Ray crystallographic studies

Suitable crystals of **3**, **4** and **6** were sealed in thin-walled glass capillaries under nitrogen atmosphere and mounted on a Bruker AXS SMART 1000 diffractometer. Intensity data were collected in 1350 frames with increasing ω (width of 0.3° per frame). The absorption correction was based on the symmetry equivalent reflections using the SADABS program. The space group determination was based on a check of the Laue symmetry and systematic absences, and was confirmed from the structure solution. The structure was solved by direct methods using a SHELXTL package.²² All non-H atoms were located from successive Fourier maps and hydrogen atoms were refined using a riding model. Anisotropic thermal parameters were used for all non-H atoms and fixed isotropic parameters were used for H atoms.²³ Crystallographic data for **3**, **4** and **6** are summarized in Table 1.

CCDC reference numbers 207225 (**3**), 207226 (**4**) and 197793 (**6**).

See http://www.rsc.org/suppdata/dt/b3/b311113j/ for crystallographic data in CIF or other electronic format.

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