Homogeneous Catalysis

Activity of SPANphos Rhodium Dimers in Methanol Carbonylation**

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Oxidative addition to organometallic compounds is one of the key elementary steps in many catalytic processes. For this reason, the reaction has been extensively studied, and in the

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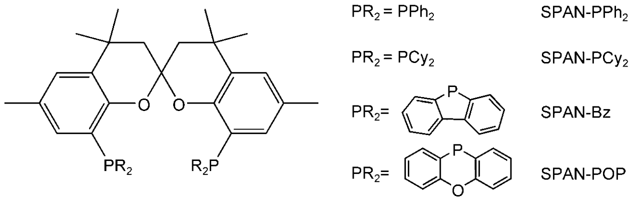
last few years many publications have appeared concerning its implication to ligand-promoted methanol carbonylation.[1] It is commonly accepted that the rate-limiting step of this reaction is precisely the oxidative addition of MeI to a square planar d^8 complex. This reaction is thought to proceed by an S$_N$2 mechanism. Accordingly, many groups have been working on the acceleration of the overall catalytic reaction by using ligands that increase the electronic density on the metal center as well as stabilizing the ligand through chelation to make it resistant to the harsh conditions of the process.[2] Recent breakthroughs on this topic concern the use of benzoic acid-based flexible *trans*-chelating diphosphines and the use of bis(imino)carbazolide ligands recently reported by Haynes and co-workers, which, to our knowledge, led to the fastest systems published until now.[3,4]

Herein we report on SPANphos mononuclear rhodium complexes, which, even though they resemble the commonly accepted catalyst precursor for methanol carbonylation with phosphine ligands, do not undergo oxidative addition with methyl iodide. As an alternative, we present unprecedented reactivity of SPANphos dinuclear complexes and its implication to the reaction mechanism of the carbonylation of methanol.

Recently, our group reported a *trans*-spanning diphosphine ligand (SPANphos, Scheme 1)[5] for which crystal structures of its mono- and dinuclear rhodium chloro carbonyl complexes have been characterized by X-ray diffraction (Figure 1).[6] These systems are closely related to the those published by Süss-Fink and co-workers and the dinuclear SPANphos rhodium compound resembles the bis-acyl complexes isolated at the end of the reaction by that group.[3] These binuclear complexes, which are formed by the elimination of phosphine, were considered to be inactive but act as a reservoir to the mononuclear, putative catalyst.[3]



Scheme 1. The SPAN-diphosphine family. Cy = cyclohexyl

Inspired by these results, we considered using complexes of SPANphos ligands, which is a truly *trans*-chelating diphosphine family that cannot *cis* coordinate, as a catalyst for methanol carbonylation. The results obtained showed that SPAN-diphosphines are very active catalyst for this reaction (Table 1). The TOF obtained compare well with those reported by Süss-Fink and co-workers for other *trans*-chelating diphosphine ligands under the same catalytic conditions.[3] In their report, the catalytic cycle is proposed to proceed through a mononuclear species that contains diphosphine ligands in a *trans* disposition.[3]

When a MeOH/rhodium ratio of about 10000:1 was used (Table 1 entries 6–11), high activities were still observed. These results can be considered as an indication that the

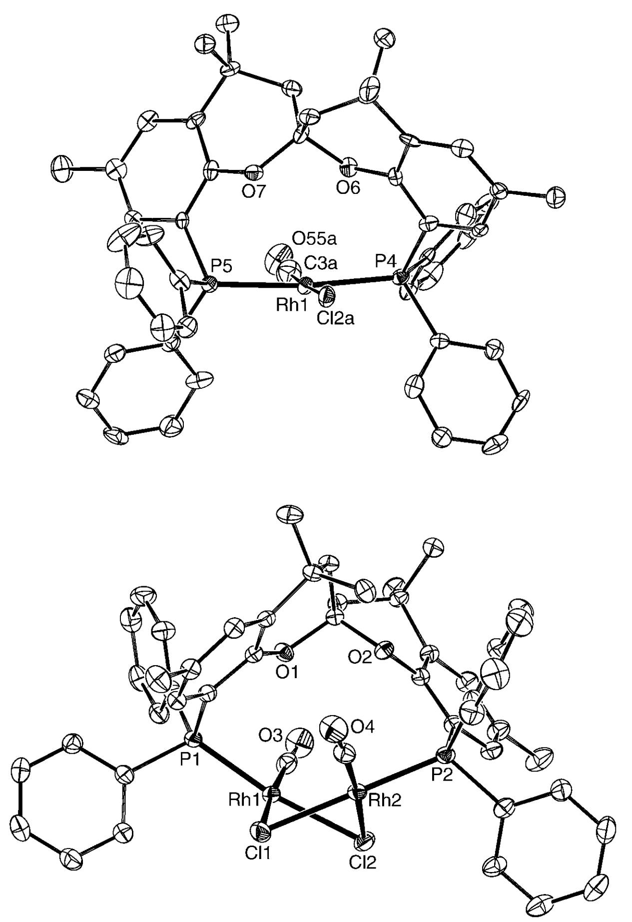


Figure 1. Upper: Displacement ellipsoid plot (50% probability level) of [RhCl(SPAN-PPh$_2$)(CO)] (**1**). The Cl and CO groups are substitutionally disordered; only the major configuration is shown. Hydrogen atoms are omitted for clarity. Lower: Displacement ellipsoid plot (50% probability level) of [Rh$_2$(μ-Cl)$_2$(SPAN-PPh$_2$)(CO)$_2$] (**2**). Hydrogen atoms and disordered CH$_2$Cl$_2$ solvent molecules have been omitted for clarity.

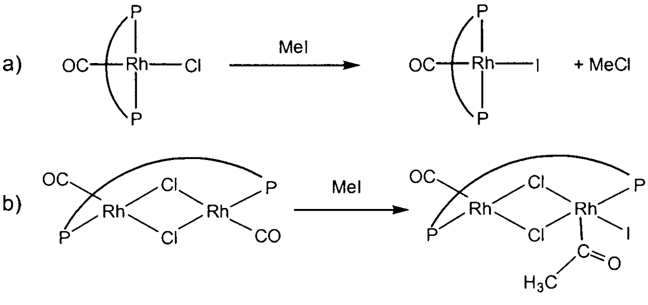
Table 1: Methanol carbonylation with Rh catalyst and SPAN-diphosphine ligands.[a]

Entry	Ligand[b]	Conv. [%]	*t* [h]	TON[c]	TOF[d]
1[e]	no ligand	20	0.25	190	762
2[e]	SPAN-PPh$_2$	93	1	902	902
3[e]	SPAN-PCy$_2$	86	0.67	831	1247
4[e]	SPAN-Bz	84	0.67	817	1225
5[e]	SPAN-POP	79	0.3	766	2299
6[f]	no ligand	no conv.	1.5	0	0
7[f]	SPAN-PPh$_2$	11.3	1.5	1093	728
8[f]	SPAN-PCy$_2$	9.1	1.5	880	586
9[f]	SPAN-Bz	9.1	1.5	880	586
10[f]	SPAN-POP	7.5	1.5	725	483
11[f,g]	SPAN-POP	14.3	1.5	2764[g]	1842[g]

[a] Conditions: T = 150 °C, P(at 22 °C) = 22 bar of CO, 700 rpm, [{Rh(μ-Cl)(CO)$_2$}$_2$] 28 μmol, ligand/Rh = 1. [b] PPh$_2$, PCy$_2$, Bz, and POP refer to the substitution of the phosphorous atom (see Scheme 1). [c] TON = turnover number (in mol conversion per mol Rh). [d] TOF = turnover frequency (in mol conversion per mol Rh per h). [e] MeOH/MeI/H$_2$O/Rh = 967:100:682:1. [f] MeOH/MeI/H$_2$O/Rh = 9670:1000:6820:1. [g] Dimeric [Rh$_2$(μ-Cl)$_2$(SPAN-POP)(CO)$_2$], ligand/Rh = 1:2, TON in mol conversion per mol Rh$_2$, TOF in mol conversion per mol Rh$_2$ per h.

observed activity cannot be just attributed to a medium effect caused by phosphine quaternization taking place during the reaction.

Surprisingly, the study of the rate of the oxidative addition of MeI to the mononuclear [ClRh(SPAN-PPh$_2$)(CO)] (**1**) rendered no rhodium(III) methyl or acetyl compounds, not even after 24 h in pure MeI. Only [RhI(SPAN-PPh$_2$)(CO)], which arises from halide metathesis, was isolated at the end of the reaction (Scheme 2, reaction a). A previously reported example of halide exchange instead of oxidative addition was found for a *cis* coordinated mixed P,S-bidentate ferrocenyl ligand.[7] A crystal structure examination of the corresponding [RhCl(CO)(L)] complex showed that one face of the square planar complex is blocked by the ferrocenyl moiety of the ligand backbone, thus inhibiting MeI addition.[7] Both of these cases can be considered as an extreme situation of the extensively studied steric effects on the rate of MeI oxidative addition.[1c,8]



Scheme 2. a) Reaction of **1** with MeI. b) Reaction of **2** with MeI and the proposed structure for the resulting acyl compound; configuration at the Rh center is unclear.

When dimeric [Rh$_2$(μ-Cl)$_2$(SPAN-POP)(CO)$_2$] was tested as a catalyst for methanol carbonylation (Table 1, entry 11) the results obtained showed that this catalyst is nearly four times more active than the corresponding mononuclear compound (entry 10). These results, together with the fact that when using other *trans*-spanning diphosphines dinuclear structures were isolated at the end of the reaction,[3] brought us to consider a different approach: the activity observed in the case of *trans*-spanning diphosphine ligands should perhaps be attributed to a dinuclear species rather than to the mononuclear species, [RhX(*trans*-P-P)(CO)] (X = Cl, I). To prove this hypothesis, we studied the rate of MeI oxidative addition to the dinuclear compound **2** (Scheme 2, reaction b). The results obtained showed that the oxidative addition to this dimetal species is only ten times slower compared to the most active catalyst reported until now (Figure 2),[4] but it constitutes the most active phosphine-based catalyst. In the IR spectrum of the reaction, the fact that the band at 1981 cm^{-1} decays but does not disappear at the end of the reaction suggests that the migration, and probably also the oxidative addition, occurs only at one of the two rhodium centers. The addition of MeI at only one of the two metallic centers of a rhodium dimer to render a Rh^{I}–Rh^{III} monoacyl species is not unprecedented. Similar reactivity, at much lower reaction rates, has already been reported by Oro and co-workers for dinuclear Rh complexes with diamido bridging ligands.[9] Simultaneous NMR spectroscopy experiments performed on reaction mixtures and GC–MS analysis of reaction products are consistent with this hypothesis.

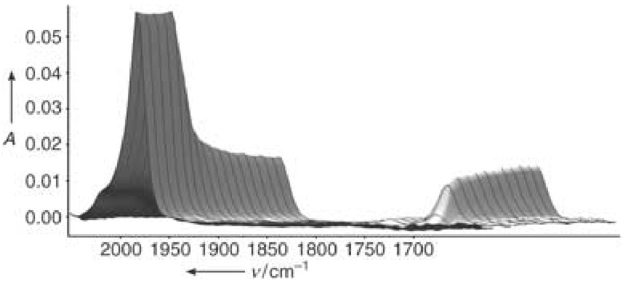


Figure 2. IR decay curves/surface for oxidative addition of MeI to **2** at 283 K. [MeI] = 1.6 M (1 spectrum per minute).

Kinetic studies by using in situ FTIR have been performed on the reaction of MeI with the dinuclear compound **2**, which showed that the reaction is first order with respect to both MeI and **2**. From the pseudo first-order constants obtained over a range of MeI concentrations and temperatures, the activation parameters ($\Delta H^{+} = 32.15\ \text{kJ mol}^{-1}$, $\Delta S^{+} = -163.73\ \text{J mol}^{-1}\text{K}^{-1}$) were calculated. These values are in concordance with those previously reported for this reaction with mononuclear complexes.[1c,4,8a,8b]

We conclude that *trans*-spanning diphosphine ligands form mononuclear rhodium compounds that are inactive for the oxidative addition of methyl iodide. The lack of reactivity as established for SPAN-diphosphines should be attributed to one face of the square-planar compound being completely blocked by the backbone of the ligand. Consequently, the activity observed with mononuclear systems as precursors for MeOH carbonylation is most likely to arise from dinuclear species formed by partial dissociation of the ligand. A complete catalytic cycle that involves dinuclear species should be considered. These dimetal compounds showed an unprecedented activity for MeI oxidative addition, and also for MeOH carbonylation, and constitute one of the fastest systems reported until now.

Experimental Section

SPAN-diphosphines were synthesized according to a modified reported procedure published for the diphenyl phosphine derivative.[5]

Compounds **1** and **2** were synthesized in Schlenk tubes by mixing the appropriate quantities of SPAN-PPh$_2$ and [Rh$_2$(μ-Cl)$_2$(CO)$_4$], dissolving the mixtures in degassed CH$_2$Cl$_2$, passing the resulting solutions through celite, and removing the solvent by evaporation. Yields were quantitative. Suitable crystals for X-ray diffraction were grown by slow diffusion of pentane into CH$_2$Cl$_2$ solutions of the rhodium complexes.

1: ^{1}H NMR (400 MHz, 298 K, CD$_2$Cl$_2$, TMS): $\delta = 1.22$ (s, 3H, CH$_3$), 1.24 (s, 3H, CH$_3$), 1.31 (s, 6H, CH$_3$), 1.77 (d, $J = 13.8$ Hz, 1H, CH$_2$), 1.86 (d, $J = 13.8$ Hz, 1H, CH$_2$), 1.96 (s, 3H, CH$_3$), 2.00 (s, 3H, CH$_3$), 2.45 (d, $J = 13.8$ Hz, 1H, CH$_2$), 2.49 (d, $J = 13.8$ Hz, 1H, CH$_2$), 6.23 (dd, $J = 9.6$, $J = 1.6$ Hz, 1H, CH$_{\text{arom}}$), 6.40 (dd, $J = 9.6$, $J = 1.6$ Hz, 1H, CH$_{\text{arom}}$), 7.01 (d, $J = 1.6$ Hz, 1H, CH$_{\text{arom}}$), 7.02 (d, $J = 1.6$ Hz, 1H, CH$_{\text{arom}}$), 7.15–7.45 (m, 16H, CH$_{\text{arom}}$), 7.72 (dd, $J = 9.6$, $J = 8.4$ Hz, 1H, CH$_{\text{arom}}$), 7.84 ppm (dd, $J = 9.6$, $J = 8.4$ Hz, 1H, CH$_{\text{arom}}$); ^{13}C NMR

(100 MHz, 298 K, TMS): $\delta = 21.4$ (CH_3), 21.5 (CH_3), 29.3 (CH_3), 29.5 (CH_3), 30.6 (CH_3), 30.8 (CH_3), 47.9 (CH_2), 48.1 (CH_2), 86.3 (C), 86.5 (C), 117.2 (C), 127–138 ppm (C_{arom}); ^{31}P NMR (162 MHz, 298 K): $\delta = 22.29$ (dd, $J = 365.4$, $J = 132.0$ Hz), 26.50 ppm (dd, $J = 365.4$, $J = 132.0$ Hz); MS [$M-$Cl].

2: ^1H NMR(400 MHz, 298 K, CD_2Cl_2, TMS): $\delta = 0.73$ (s, 3H, CH_3), 1.18 (s, 3H, CH_3), 1.70 (d, $J = 14.4$ Hz, 1H, CH_2), 2.00 (s, 3H, CH_3), 2.10 (d, $J = 14.4$ Hz, 1H, CH_2), 6.28 (dd, $J = 12.0$, $J = 1.6$ Hz, 1H, CH_{arom}), 7.05 (d, $J = 1.5$ Hz, 1H, CH_{arom}), 7.15–7.35 (m, 8H, CH_{arom}), 7.73 ppm (dd, $J = 11.6$, $J = 7.6$ Hz, 1H, CH_{arom}); ^{13}C NMR (100 MHz, 298 K, TMS): $\delta = 21.1$ (CH_3), 29.5 (CH_3), 31.0 (d, CH_3, $J = 20.6$ Hz), 50.462 (CH_2), 102.5 (C), 117.2 (C), 128–137 ppm (C_{arom}); ^{31}P NMR (162 MHz, 298 K): $\delta = 45.88$ ppm (d, $J = 178.16$ Hz); MS [$M-$Cl], [$M-2$Cl].

Catalytic experiments: In a typical experiment 29.3 mL of a mixture MeOH/H_2O was placed in a 100-mL Hastelloy autoclave. The autoclave was then pressurized to 10 bar of carbon monoxide and heated to 150 °C with vigorous stirring (700 rpm). When the reaction temperature was reached and had stabilized, a solution of [$Rh_2Cl_2(CO)_4$] and the appropriate quantity of the corresponding ligand in MeI were added through a liquid injection port and the autoclave was pressurized to the desired reaction pressure. Pressure was maintained constant during the reaction by feeding gas from a 1-L autoclave pressurized with over 60 bar of carbon monoxide. After the required reaction time, the autoclave was cooled to room temperature. The solution was analyzed by NMR spectroscopy to determine the selectivity. The conversion was calculated from gas consumption of the reservoir autoclave.

Kinetic experiments: Kinetic measurements for the reaction of **1** or **2** with MeI in CH_2Cl_2 were performed in situ by using a React IR 4000 from Mettler Toledo equipped with a diamond probe. A solution that contained the corresponding rhodium compound in distilled CH_2Cl_2 was placed in the sample vessel under an argon atmosphere. The temperature was fixed by using a thermostat jacket. When the desired temperature was achieved and remained constant, freshly distilled MeI was added by using a syringe. The IR spectra were scanned in the region 400–2200 cm^{-1} and saved at regular time intervals (usually 10 s) under computer control.

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[6] a) Crystal structure determinations: X-ray intensities were measured on a Nonius KappaCCD diffractometer with a rotating anode (graphite monochromator, $\lambda = 0.71073$ Å) at 150 K. The structures were solved with direct methods (SHELXS-97)[6b] and refined with SHELXL-97[6b] against F^2 of all reflections. Structure calculations and checking were performed with the PLATON program.[6c] Compound **1**: $C_{48}H_{46}ClO_3P_2Rh$, $M_r = 871.15$, yellow needles, $0.18 \times 0.12 \times 0.06$ mm^3, orthorhombic, $Pna2_1$ (no. 33), $a = 17.271(2)$, $b = 13.1760(12)$, $c = 17.5576(18)$ Å, $V = 3995.4(7)$ Å^3. $Z = 4$, $\rho_{calcd} = 1.448$ gcm^{-3}. A total of 50605 reflections were measured of which 7749 were unique. The crystal appeared to be cracked into two fragments with a rotation of 4° approximately about the *a* axis. The structure was thus refined as a general twin of two domains with a twin fraction of 0.284(2). The CO and Cl ligands were substitutionally disordered to each other in a ratio of 0.62:0.38, respectively; 524 parameters, 4 restraints; *R* values: *R*1 ($I > 2\sigma(I)$): 0.0566, *wR*2 (all refl.) = 0.1096; Flack *x* parameter $-0.06(4)$; $S = 1.080$. Compound **2**: $C_{49}H_{46}Cl_2O_4P_2Rh_2 \cdot 2CH_2Cl_2$, $M_r = 1207.37$, orange plates, $0.35 \times 0.33 \times 0.12$ mm^3, monoclinic, $P2_1/c$ (no. 14), $a = 19.7446(1)$, $b = 14.4777(1)$, $c = 19.2880(1)$ Å, $\beta = 110.1247(2)°$, $V = 5176.97(5)$ Å^3. $Z = 4$, $\rho_{calcd} = 1.549$ gcm^{-3}. A total of 79995 reflections were measured of which 11842 were unique. The CH_2Cl_2 solvent molecules were disordered; 620 parameters, 69 restraints; *R* values: *R*1 ($I > 2\sigma(I)$): 0.0279, *wR*2 (all refl.) = 0.0747; $S = 1.043$. CCDC-260236 (**1**) and -260237 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif; b) G. M. Sheldrick, SHELXS-97 and SHELXL-97, programs for crystal structure solution and refinement, University of Göttingen, Germany, **1997**; c) A. L. Spek, *J. Appl. Crystallogr.* **2003**, *36*, 7–13.

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