DOI: 10.1002/ejic.201100423

Dicarbonylrhodium(I) Complexes of Bipyridine Ligands with Proximate H-Bonding Substituents and Their Application in Methyl Acetate Carbonylation

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Keywords: Carbonylation / Rhodium / Acetic acid / Methanol / Carbon monoxide / Homogeneous catalysis

A series of cationic *cis*-dicarbonylrhodium(I) complexes $[Rh(L)(CO)_2]SbF_6$ has been prepared containing 2,2′-bipyridine ligands with proximate H-bonding substituents R in the 6- and 6′-position (R = OH, NH_2, COOEt and $PO(OEt)_2$). The solid-state structures have been determined by X-ray crystallography for the complexes where R = OH, NH_2 and COOEt. The molecular structures have revealed metal–metal and π–π interactions between the square-planar complexes resulting in the formation of molecular chains in the solid state. IR studies on the reaction of $[Rh(bipy)(CO)_2]SbF_6$ with MeI have shown the formation of a neutral complex [RhI(CO)(bipy)], which undergoes oxidative addition of MeI much faster than the cationic complex $[Rh(bipy)(CO)_2]^+$. Although all complexes show good activities for the carbonylation of methyl acetate, this is believed to be due to their instability and the formation of $[RhI_2(CO)_2]^-$ under the reaction conditions.

Introduction

The carbonylation of methanol is currently the most important industrial process for the large-scale production of acetic acid.[1,2] Annual production capacity is ca. 7 million tons worldwide and continues to grow, especially in Asia.[3] The first commercial methanol carbonylation plants were operated by BASF in the 1960s, and the initial catalysts were based on cobalt.[4] These were quickly superseded by a rhodium-catalysed process, which was developed by Monsanto in the 1970s.[5,6] In the 1990s BP introduced the Cativa process based on iridium, and this is currently the preferred catalyst technology for new acetic acid plants.[7,8] All catalyst systems require iodide as a co-catalyst for the activation of methanol (or methyl acetate) to generate methyl iodide. Methyl iodide reacts with the transition-metal catalyst by oxidative addition to form a metal–methyl bond, which can subsequently undergo CO insertion followed by the reductive elimination of acetyl iodide and hydrolysis to acetic acid.[9] In the rhodium-catalysed process, the rate of carbonylation is first order in iodide concentration due to a relatively slow oxidative addition reaction. In contrast, for the iridium-catalysed process, the rate of carbonylation shows an inverse relation to the iodide concentration, and the concentration of free iodide in the system needs to be carefully controlled through the use of additional promoters.[8,10–14] Alternative strategies for the activation of methanol have used strong acids such as zeolites,[15–18] heteropolyacids[19] and superacids.[20] These strong acids can protonate methanol, which upon elimination of H_2O generates the carbenium cation, CH_3^+.[18,20] Although these strong acids can carbonylate methanol without the presence of a transition metal, the selectivities are generally lower due to the formation of significant amounts of dimethyl ether.[19,21,22]

The high temperatures and the strongly acidic reaction conditions required for methanol carbonylation, combined with the use of iodide as the co-catalyst, present significant challenges in terms of reactor engineering and corrosion prevention. Alternative catalysts that can operate under milder reaction conditions could significantly lower the cost of acetic acid production. To this end, during the last decade several groups have investigated the use of group 9 metal complexes containing a range of ligands as catalysts for methanol carbonylation.[23] Examples are the application of monodentate[24,25] and bidentate phosphane ligands[26–33] as well as cyclopentadienyl ligands[34,35] and combinations thereof.[36] Nitrogen-based ligands such as diimines and pyridine ligands have also been investigated.[37–39] Noteworthy, Dutta and co-workers have recently reported improved catalytic behaviour of rhodium catalysts for methanol carbonylation, when monodentate pyridine ligands with carboxylic acid substituents were employed.[40]

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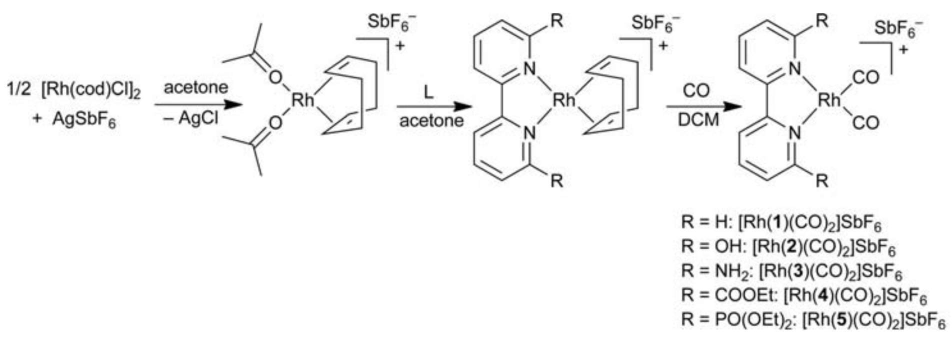
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201100423.

The coordination chemistry of ligands with proximate acidic or basic functionalities and their application in homogeneous catalysis has been an ongoing theme in our laboratory. Previously, we have reported on the application of such ligands in the context of alkane oxidation,[41–43] and very recently we have communicated our first results on methyl acetate carbonylation.[44] Here we present the synthesis and characterisation of a series of novel dicarbonylrhodium(I) complexes [Rh(L)(CO)$_2$]SbF$_6$ containing 2,2′-bipyridine ligands with Brønsted-acidic H-bonding substituents in the 6- and 6′-position (see Figure 1), with a view to activate the methyl acetate substrate in the vicinity of the metal centre. The functionalities investigated in this study cover a range of pK_a values, from weakly acidic OH groups (cf. PhOH, pK_a = 10.0) to ammonium NH$_3^+$ (cf. PhNH$_3^+$, pK_a = 4.6), carboxylic acid COOH (cf. PhCOOH, pK_a = 4.2) to moderately acidic phosphonic acid functionalities PO(OH)$_2$ [cf. PhPO(OH)$_2$, pK_{a1} = 2.1]. In the case of 6,6′-dihydroxy-2,2′-bipyridine (**2**), the acidic OH functionalities are present in the starting complex, whereas in the other complexes the acidic functionality is generated in situ, either by protonation of the amine substituents of 6,6′-diamino-2,2′-bipyridine (**3**), or by transesterification of the esters under acidic conditions in the case of ligands **4** and **5**. The catalytic activity of the functionalised complexes for the carbonylation of methyl acetate to give acetic acid or acetic anhydride has been investigated. Furthermore, the oxidative addition reaction of MeI has been studied in greater detail for complex [Rh(**1**)(CO)$_2$]SbF$_6$, and the stability of the complexes under carbonylation conditions has been evaluated.

Results and Discussion

Synthesis of Ligands and Complexes

The preparation of cationic dicarbonylrhodium(I) complexes of the type [Rh(bipy)(CO)$_2$]$^+$ (bipy = 2,2′-bipyrdine) was first reported by Reddy and Ramesh.[45] In this study, the complexes [Rh(L)(CO)$_2$]SbF$_6$ have been prepared according to a synthetic procedure developed by Oro and coworkers for the synthesis of similar rhodium complexes.[46] The starting material [Rh(cod)Cl]$_2$ (cod = 1,5-cyclooctadiene) was treated with AgSbF$_6$ in acetone, followed by the addition of the bipyridine ligand to give the intermediate complexes [Rh(L)(cod)]SbF$_6$. These complexes were subsequently treated with CO at room temperature to give the series of complexes of the type [Rh(L)(CO)$_2$]SbF$_6$, as shown in Equation (1).



(1)

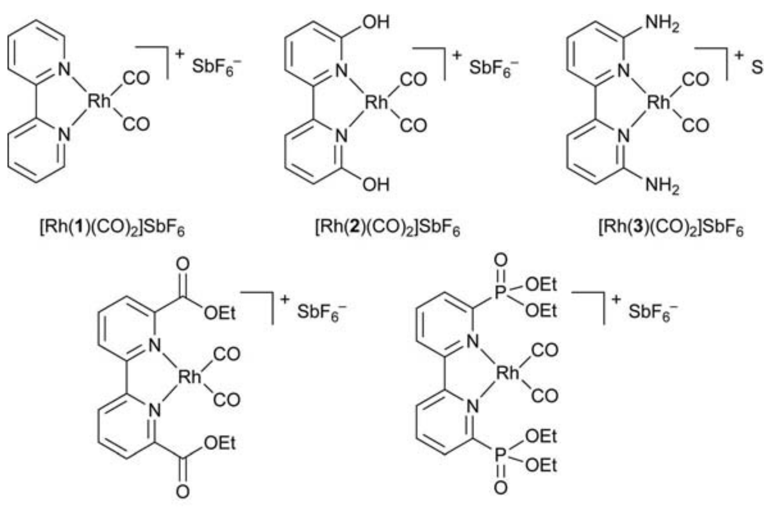


Figure 1. Cationic dicarbonylrhodium(I) complexes used as carbonylation catalysts.

Complexes [Rh(**1**)(CO)$_2$]SbF$_6$ and [Rh(**3**)(CO)$_2$]SbF$_6$ were prepared according to this method by using bipyridine (**1**) and 6,6′-diaminobipyridine (**3**), respectively. We recently communicated the preparation of complex [Rh(**2**)(CO)$_2$]SbF$_6$ from 6,6′-dihydroxy-2,2′-bipyridine (**2**), which normally exists as its tautomer 2,2′-bipyridone. This tautomer was therefore converted to 6,6′-bis(*tert*-butyldimethylsiloxy)-2,2′-bipyridine, which is easily hydrolysed after coordination to the rhodium centre to give the target complex [Rh(**2**)(CO)$_2$]SbF$_6$.[44] A number of metal complexes containing bipyridine ligands with hydroxy substituents in various positions have been reported, for example 3,3′- and 4,4′-dihydroxy-2,2′-bipyridine[47,48] and also 6-hydroxy-2,2′-bipyridine;[49] but, to the best of our knowledge, [Rh(**2**)(CO)$_2$]SbF$_6$ is the first metal complex containing the 6,6′-dihydroxy-2,2′-bipyridine ligand.

Initial attempts to prepare dicarbonylrhodium(I) complexes with 2,2′-bipyridine-6,6′-dicarboxylic acid as the ancillary ligand were hampered by the low solubility of the free acid in common organic solvents. We therefore resorted to the use of the diester derivative **4**, as it was anticipated that under the acidic carbonylation conditions, transesterification would occur. This was confirmed by monitoring the reaction of complex [Rh(**4**)(CO)$_2$]SbF$_6$ at 100 °C in CD$_3$COOD by ^{1}H NMR spectroscopy (vide infra). The reaction of the diene complex [Rh(**4**)(cod)]SbF$_6$ with CO in CH$_2$Cl$_2$ resulted in the substitution of the 1,5-cyclooctadiene ligand with CO ligands to give [Rh(**4**)(CO)$_2$]SbF$_6$. However, unlike the substitution reactions with ligands **1**–**3**, it was observed by ^{1}H NMR spectroscopy that this substitution reaction is reversible, and evaporation of the solvent at the end of the reaction resulted in the loss of CO and regeneration of the starting complex [Rh(**4**)(cod)]SbF$_6$. The complex [Rh(**4**)(CO)$_2$]SbF$_6$ could eventually be isolated from a CO-saturated CH$_2$Cl$_2$ solution by precipitation with hexane. It thus appears that the CO ligands are much more labile in this complex compared to the complexes of ligands **1**–**3**.

The tetraethyl ester of 2,2′-bipyridine-6,6′-diphosphonic acid (**5**) was employed for the synthesis of complex [Rh(**5**)(cod)]SbF$_6$. This complex does not react with CO in CH$_2$Cl$_2$ at room temperature. However, heating the complex [Rh(**5**)(cod)]SbF$_6$, suspended in CO-saturated toluene at 80 °C for 5 h resulted in the formation of the dicarbonyl complex [Rh(**5**)(CO)$_2$]SbF$_6$. All complexes were characterised by multinuclear NMR and IR spectrosopy, mass spectrometry, and microanalysis. The solid-state structures of complexes [Rh(**2**)(CO)$_2$]SbF$_6$, [Rh(**3**)(CO)$_2$]SbF$_6$ and [Rh(**4**)(CO)$_2$]SbF$_6$ have been determined by X-ray crystallography.

Complex Stability

Typical carbonylation conditions for the Monsanto and Cativa process involve temperatures up to 200 °C and pressures up to 50 bar, and the current catalysts, [RhI$_2$(CO)$_2$]$^-$ and [IrI$_2$(CO)$_2$]$^-$, are stable under these conditions. In order to evaluate the stability of our new complexes under the carbonylation reaction conditions, solutions of the complexes [Rh(**3**)(CO)$_2$]SbF$_6$, [Rh(**4**)(CO)$_2$]SbF$_6$ and [Rh(**5**)(CO)$_2$]SbF$_6$ in CD$_3$COOD at 100 °C were monitored by ^{1}H NMR spectroscopy over time (see Figures S15–S19). The amino-substituted complex [Rh(**3**)(CO)$_2$]SbF$_6$ has a half-life of ca. 1 d under these conditions, decomposing slowly to a multitude of species. Complexes [Rh(**4**)(CO)$_2$]SbF$_6$ and [Rh(**5**)(CO)$_2$]SbF$_6$ have half-lives of approximately 12 h and 4 h, respectively, and show the formation of ethyl acetate under these conditions, which suggests that the aforementioned transesterification does indeed take place.

Solid-State Structures

Square-planar d^8 Rh^I complexes are known to form Rh^I–Rh^I interactions in the solid state resulting in one-dimensional molecular chains.[50,51] These metal–metal interactions, together with π–π interactions between the ligands, give rise to unusual optical and electrical properties, which make these materials of interest for example as molecular wires.[52,53] The solid-state structures of the rhodium(I) complexes studied here have been analysed in detail as they all show intermolecular interactions in the solid state.

The solid-state structure of [Rh(**2**)(CO)$_2$]SbF$_6$ was already discussed in detail in our recent communication.[44] For comparison with the other structures, the main features are described briefly. The structure was found to contain five crystallographically independent molecules A–E in the asymmetric unit; complex [Rh(**2**)(CO)$_2$]SbF$_6$-A is shown in Figure 2 (see Table 1 for bond lengths and angles). Each complex is nearly planar, and the close Rh···Rh separations between 3.28 and 3.33 Å, together with Rh···Rh···Rh angles between 172 and 178° result in molecular chains. Within these chains there are significant π–π interactions between the pyridyl rings of adjacent complexes, and in each case the rings are inclined by less than 2°.

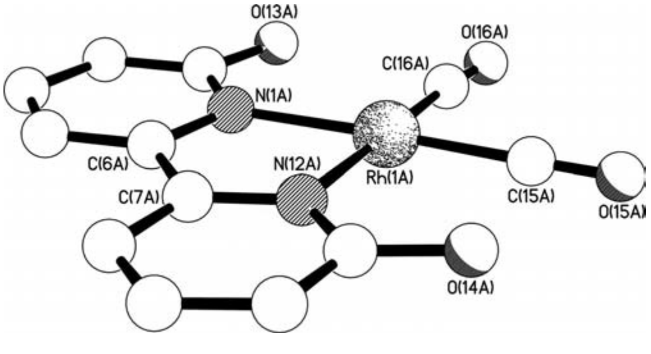


Figure 2. Molecular structure of [Rh(**2**)(CO)$_2$]SbF$_6$-A, one of the five crystallographically independent cationic complexes present in the crystals of [Rh(**2**)(CO)$_2$]SbF$_6$.[44]

The NH$_2$-substituted complex [Rh(**3**)(CO)$_2$]SbF$_6$ shows a folded geometry whereby the {N(1),C(6),C(7),N(12)} and {N(1),N(12),Rh} planes are inclined by ca. 29° (see Figure 3 and Table 2 for selected bond lengths and angles). This appears to be a consequence of the different steric

Table 1. Selected bond lengths [Å] and angles [°] for the five independent complexes A–E present in the crystals of [Rh(**2**)(CO)$_2$]SbF$_6$.

	A	B	C	D	E
Rh(1)–N(1)	2.088(6)	2.092(7)	2.101(6)	2.070(6)	2.091(6)
Rh(1)–N(12)	2.102(6)	2.082(7)	2.067(6)	2.064(6)	2.089(6)
Rh(1)–C(15)	1.880(8)	1.842(10)	1.845(8)	1.847(10)	1.862(8)
Rh(1)–C(16)	1.900(10)	1.861(9)	1.853(10)	1.829(10)	1.843(9)
N(1)–Rh(1)–N(12)	78.3(2)	78.0(3)	78.4(3)	77.9(3)	78.3(3)
N(1)–Rh(1)–C(15)	177.0(3)	177.2(3)	175.9(3)	176.5(3)	176.5(3)
N(1)–Rh(1)–C(16)	98.7(3)	98.1(3)	99.7(4)	99.8(3)	98.8(3)
N(12)–Rh(1)–C(15)	98.8(3)	99.3(3)	97.6(3)	98.7(4)	99.5(3)
N(12)–Rh(1)–C(16)	176.1(3)	176.1(3)	177.8(4)	177.6(3)	177.2(3)
C(15)–Rh(1)–C(16)	84.3(4)	84.6(4)	84.3(4)	83.5(4)	83.3(4)

requirements of the NH$_2$ vs. OH substituents. Adjacent C_i-related complexes stack through a pair of π–π interactions between ring A in one complex and ring B in the next one (interaction a in Figure 4) with centroid···centroid and mean interplanar separations of ca. 3.72 and 3.40 Å, respectively; the two rings are inclined by ca. 12°. These pairs of complexes are approached by C_2-related pairs and are loosely held together by π–π interactions between rings A and B in neighbouring pairs (interaction b in Figure 4) with centroid···centroid and mean interplanar separations of ca. 4.09 and 3.32 Å, respectively; the two rings are inclined by ca. 22°. The combination of these π–π interactions results in a chain of complexes extending along the crystallographic *a*-axis direction. All four N–H protons in the structure of [Rh(**3**)(CO)$_2$]SbF$_6$ are involved in N–H···F hydrogen bonds to the SbF$_6$ anion as shown in Figure 3.

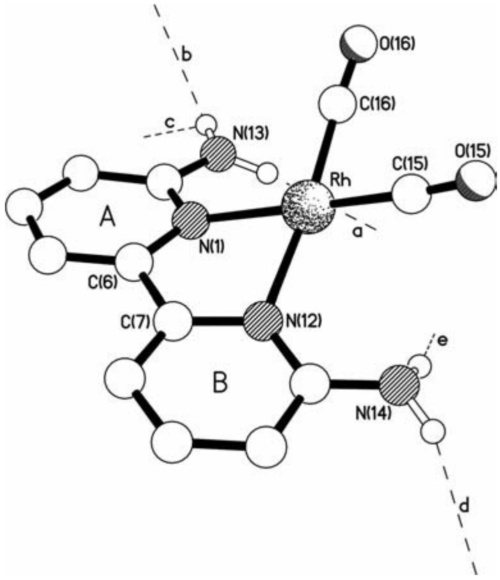


Figure 3. Molecular structure of the cation in [Rh(**3**)(CO)$_2$]SbF$_6$ showing the N–H···F hydrogen bonding interactions. The N···F and H···F distances, and the N–H···F angles [°] are (a) 3.025(2), 2.13, 172; (b) 3.121(3), 2.37, 142; (c), 3.124(2), 2.39, 139; (d) 3.077(2), 2.21, 161; (e) 3.000(2), 2.12, 166.

The structure of complex [Rh(**4**)(CO)$_2$]SbF$_6$ was found to contain two crystallographically independent molecules in the asymmetric unit: [Rh(**4**)(CO)$_2$]SbF$_6$-A (shown in Figure 5) and [Rh(**4**)(CO)$_2$]SbF$_6$-B (in Figure S22) (bond lengths and angles are collected in Table 3). The cationic complex adopts a similar folded conformation to that seen for complex [Rh(**3**)(CO)$_2$]SbF$_6$, with the {N(1),C(6),C(7),N(12)} and {N(1),N(12),Rh} planes being inclined by ca. 27 and 25° for complexes A and B, respectively. Accompanying these folds are twists of the ester moieties out of the pyridine plane by ca. 24, 27, 39 and 31° for the O(13A), O(14A), O(13B) and O(14B) groups, respectively. In each case, the carbonyl oxygen atom is pointing towards the metal centre, minimising the steric repulsion between the metal atom and the ester groups. The two complexes stack in an alternating ···A···B···A···B··· fashion

Table 2. Selected bond lengths [Å] and angles [°] for [Rh(**3**)(CO)$_2$]SbF$_6$.

Rh–N(1)	2.0766(16)	Rh–N(12)	2.0720(15)
Rh–C(15)	1.865(2)	Rh–C(16)	1.874(2)
N(1)–Rh–N(12)	77.62(7)	N(1)–Rh–C(15)	171.13(8)
N(1)–Rh–C(16)	98.99(8)	N(12)–Rh–C(15)	97.59(8)
N(12)–Rh–C(16)	174.24(8)	C(15)–Rh–C(16)	85.14(9)

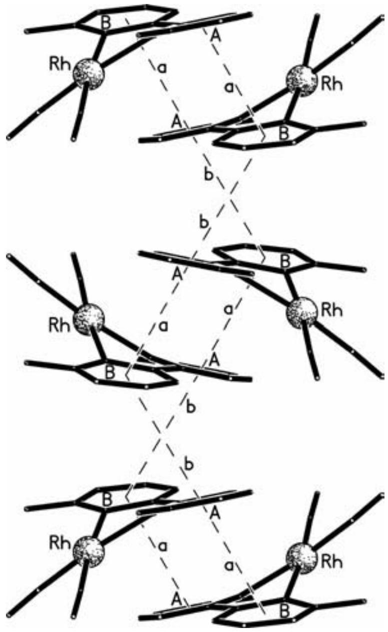


Figure 4. Part of one of the chains of π–π linked complexes along the crystallographic *a*-axis direction present in the crystals of [Rh(**3**)(CO)$_2$]SbF$_6$. The π–π interactions a and b have centroid···centroid and mean interplanar separations [Å] of (a) 3.72, 3.40, and (b) 4.09, 3.32, respectively.

Table 3. Selected bond lengths [Å] and angles [°] for the two independent complexes A and B present in the crystals of $[Rh(\mathbf{4})(CO)_2]SbF_6$.

	A	B		A	B
Rh–N(1)	2.125(6)	2.119(8)	Rh–N(12)	2.112(6)	2.147(9)
Rh–C(21)	1.862(9)	1.881(11)	Rh–C(22)	1.872(9)	1.867(11)
N(1)–Rh–N(12)	78.5(2)	78.1(4)	N(1)–Rh–C(21)	169.6(4)	173.1(4)
N(1)–Rh–C(22)	98.0(3)	98.5(4)	N(12)–Rh–C(21)	95.7(3)	99.7(4)
N(12)–Rh–C(22)	173.1(4)	172.0(4)	C(21)–Rh–C(22)	86.7(4)	82.8(5)

along the crystallographic *a*-axis direction such that the bipyridyl rings of adjacent complexes are on opposite sides (Figure 6). The most notable feature of these chains are the Rh···Rh separations of ca. 3.92 Å; the associated Rh···Rh···Rh angles are ca. 176 and 179° at RhA and RhB, respectively.

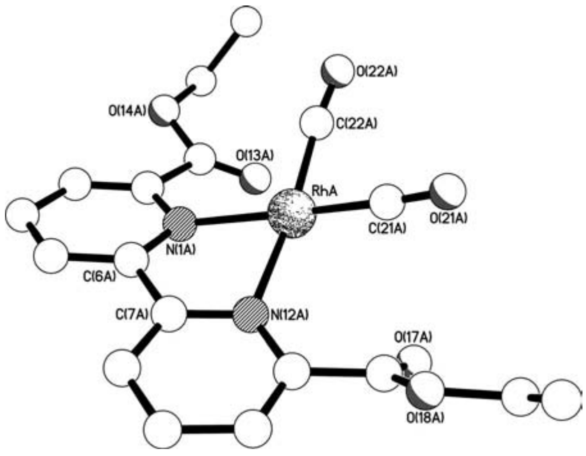


Figure 5. Molecular structure of one ($[Rh(\mathbf{4})(CO)_2]SbF_6$-A) of the two crystallographically independent cationic complexes present in the crystals of $[Rh(\mathbf{4})(CO)_2]SbF_6$.

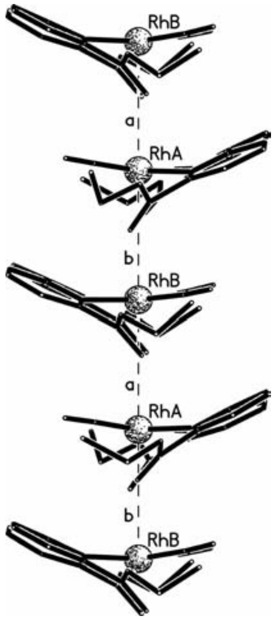


Figure 6. Part of one of the chains of complexes along the crystallographic *a*-axis direction present in the crystals of $[Rh(\mathbf{4})(CO)_2]SbF_6$. The Rh···Rh separations a and b are both ca. 3.92 Å.

Spectroscopy

The structural aspects of the series of dicarbonylrhodium(I) complexes discussed in the previous section have shown that the plane of the bipyridine ligand can form an angle with the coordination plane of the metal complex, which appears to be caused by the steric requirements of the substituents in the 6,6′-positions of the ligand.[54] The angle θ_s between the two planes defined by [N,Rh,N] and the bipyridine ligand [N,C,C,N] for all five complexes are listed in Table 4.[55] These angles are smaller than the θ_s angles observed in square-planar platinum(II) and palladium(II) complexes with similar 6,6′-dimethyl-substituted bipyridine ligands. For example, the θ_s angles in dichlorido(6,6′-dimethylbipyridine)platinum(II) and -palladium(II) complexes are 36.73(11)° and 38.84(9)°, respectively; and similar angles have been observed in (2,9-dimethylphenanthroline)palladium(II) complexes.[56] A smaller angle of 27.44(7)° was observed in the case of the dichloridopalladium(II) complex with only one 6-methyl substituent,[55] which is similar to the angles seen here for complexes $[Rh(\mathbf{3})(CO)_2]SbF_6$ and $[Rh(\mathbf{4})(CO)_2]SbF_6$.

Table 4. Geometric and spectroscopic properties of $[Rh(L)(CO)_2]SbF_6$ complexes.

Complex (see Figure 1)	θ_s[a] [°]	$\nu(CO)$[b] [cm^{-1}]	$^1J_{C\text{-}Rh}$[c] [Hz]
$[Rh(\mathbf{1})(CO)_2]SbF_6$ (R = H)		2109(s), 2095(w), 2054(s), 2025(w)	69.5
$[Rh(\mathbf{2})(CO)_2]SbF_6$ (R = OH)	2, 0, 0, 1, 2	2108(s), 2101(s), 2093(s), 2052(s), 2045(s), 2031(s)	70.9
$[Rh(\mathbf{3})(CO)_2]SbF_6$ ($R = NH_2$)	29	2097(s), 2084(w), 2035(s), 2010(w)	69.1
$[Rh(\mathbf{4})(CO)_2]SbF_6$ (R = COOEt)	27, 25	2097(s), 2079(w), 2041(s), 2005(w)	60.0
$[Rh(\mathbf{5})(CO)_2]SbF_6$ $[R = PO(OEt)_2]$		2096(s), 2033(s)	73.4

[a] Angle between the 2,2′-bipyridine ligand and the coordination plane defined by [N,C,C,N] and [N,Rh,N]. For complexes $[Rh(\mathbf{2})(CO)_2]SbF_6$ and $[Rh(\mathbf{4})(CO)_2]SbF_6$ several independent molecules are observed in the solid-state structures. [b] Measured in Nujol (s = strong, m = medium, w = weak). [c] Measured in $[D_6]$-acetone.

Selected spectroscopic features of the dicarbonylrhodium complexes containing ligands **1**–**5** are collected in Table 4. Infrared spectroscopy shows two strong absorptions for each complex in the carbonyl stretching region, as expected for square-planar *cis*-dicarbonyl complexes. The frequencies for complex $[Rh(\mathbf{1})(CO)_2]SbF_6$ are comparable to the two sets of values reported for $[Rh(\mathbf{1})(CO)_2]ClO_4$ (2108 & 2050 cm^{-1} and 2103 & 2044 cm^{-1})[45,57] However, additional bands are also observed for the complexes containing ligands **1**–**4**, which in the case of complex $[Rh(\mathbf{2})(CO)_2]SbF_6$ are almost as intense as the main bands (see Table 4 and Figures S12–S14). These additional absorptions are believed to be due to solid-state effects such as metal–metal and π–π interactions, as seen in the solid-state structures.[58] No apparent correlation can be observed between the θ_s angles and the ν(CO) values. In addition, from the last column in Table 4 it can be seen that the carbon-rhodium coupling constants $^1J_{C\text{-}Rh}$ appear to be independent of the angle θ_s.

Oxidative Addition Studies with MeI

The reactivity of methyl iodide with the bipy complex $[Rh(\mathbf{1})(CO)_2]SbF_6$ was investigated by IR spectroscopy.[59–61] $[Rh(\mathbf{1})(CO)_2]SbF_6$ was dissolved in a 3.2 M solution of MeI in acetonitrile, and the carbonyl region of the IR spectrum was monitored at 25 °C over 900 min (Figure 7). During the course of the reaction, the ν(CO) bands of $[Rh(\mathbf{1})(CO)_2]SbF_6$ at 2099 and 2040 cm^{-1} decayed with a half life of approximately 50 min. This is approximately 3000 times slower than the oxidative addition of MeI to the neutral complex $[RhI(\mathbf{1})(CO)]$ in CH_2Cl_2, based on extrapolation of the kinetic data at lower [MeI] values for that complex.[38] The IR spectra in Figure 7, which were determined in acetonitrile because of the poor solubility of the ionic complex in CH_2Cl_2, indicate that the reaction between $[Rh(\mathbf{1})(CO)_2]SbF_6$ and MeI is not a simple oxidative addition reaction. The initial decay of the reactant ν(CO) bands is accompanied by the appearance of absorptions at 2070 and 2094 cm^{-1} due to terminal CO ligands, along with bands at 1711 and 1733 cm^{-1} that are assigned to acetyl ligands. Over a longer time period, the bands at 2070 and 2094 cm^{-1} both decay (but at different rates), as does the acetyl band at 1733 cm^{-1}, while the lower-frequency acetyl band continues to grow.

To explain these observations, the mechanism shown in Scheme 1 is proposed, involving two pathways from the reactant $[Rh(\mathbf{1})(CO)_2]^+$ to an (acetyl)Rh^{III} product, $[RhI(COMe)(\mathbf{1})(NCMe)_2]^+$. In route A, oxidative addition of MeI to the reactant complex is followed by migratory CO insertion to give an (acetyl)(carbonyl)Rh^{III} species, that we propose gives rise to the ν(CO) bands at 2094 and 1733 cm^{-1}. The vacant coordination site generated by the migratory insertion step will likely be occupied by the coordinating solvent MeCN. Subsequent slow replacement of CO by MeCN would then give $[RhI(COMe)(\mathbf{1})(NCMe)_2]^+$, consistent with the observation of a sole acetyl ν(CO) band at 1711 cm^{-1} for the ultimate product.

The ν(CO) band observed at 2070 cm^{-1} corresponds to the known complex, $[RhI_2Me(\mathbf{1})(CO)]$, which has a ν(CO) value of 2071 cm^{-1} in CH_2Cl_2.[38] This (methyl)Rh^{III} species would result from oxidative addition of MeI to $[RhI(\mathbf{1})(CO)]$ (Scheme 1, route B). Formation of this neutral Rh^I complex requires replacement of a CO ligand by

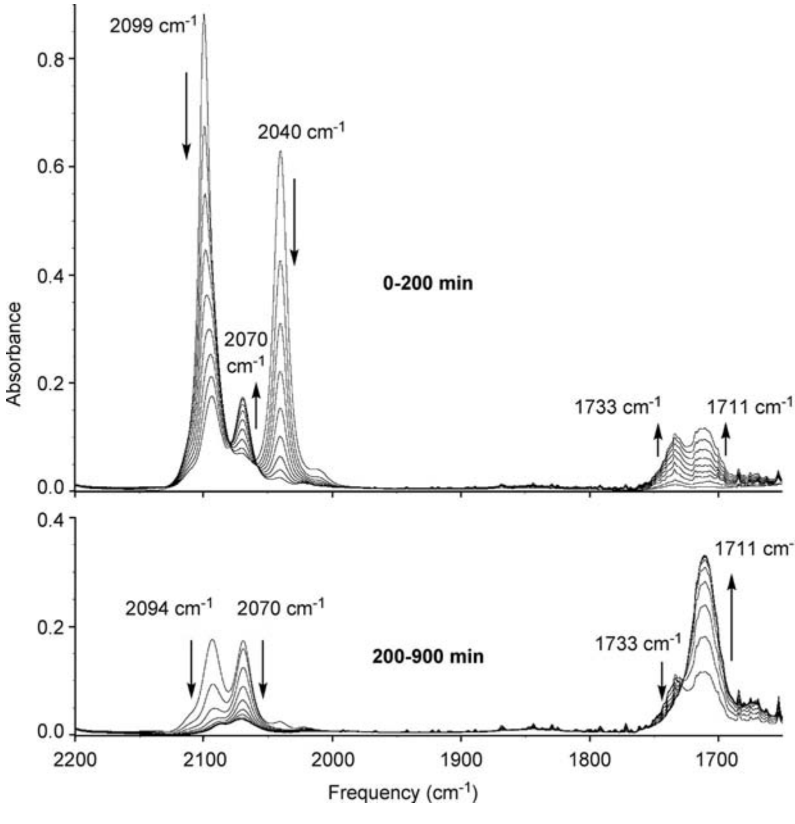
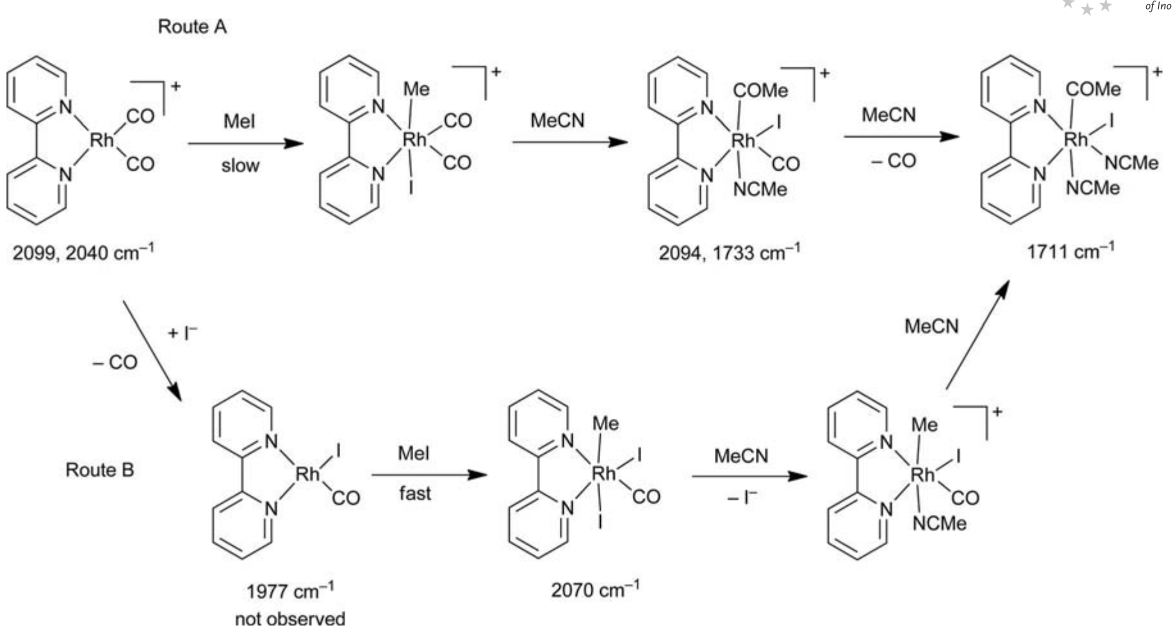


Figure 7. IR spectra obtained from the reaction between $[Rh(\mathbf{1})(CO)_2]SbF_6$ and MeI in CH_3CN at 25 °C over 900 min ([MeI] = 3.2 M).



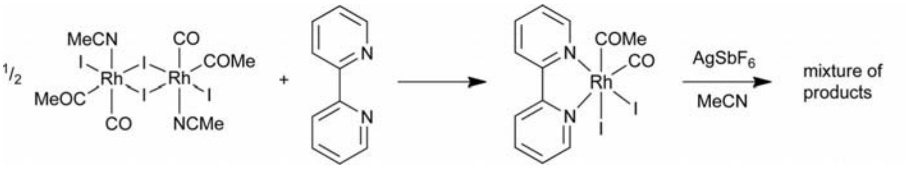
Scheme 1.

I$^-$ in the reactant complex [Rh(**1**)(CO)$_2$]$^+$, a known reaction reported previously by Mestroni et al.[62] The free I$^-$ necessary to form [RhI(**1**)(CO)] can be generated during the sequence of steps in route A, presuming that oxidative addition of MeI occurs by the conventional S$_N$2 mechanism and/or that I$^-$ can dissociate from Rh^{III} iodide species. An alternative source of free I$^-$ is the equilibrium reaction between MeCN and MeI to give [MeCNMe]$^+$ and I$^-$.[63] Once formed, [RhI(**1**)(CO)] will undergo rapid oxidative addition of MeI to give the observed [RhI$_2$Me(**1**)(CO)]. On the basis of the kinetics measured at 25 °C in CH$_2$Cl$_2$,[38] the predicted half life for this reaction with 3.2 M MeI is ca. 1 s, consistent with the nonobservation of [RhI(**1**)(CO)] [ν(CO) at 1977 cm^{-1} in CH$_2$Cl$_2$]. Haynes and co-workers found that [RhI$_2$Me(**1**)(CO)] undergoes migratory CO insertion only very slowly in CH$_2$Cl$_2$, giving small amounts of an acetyl product.[38] Over 15 h in MeCN, the ν(CO) band at 2070 cm^{-1} due to [RhI$_2$Me(**1**)(CO)] decays almost completely (Figure 7). It is proposed that substitution of iodide by MeCN gives a cationic complex that undergoes migratory CO insertion more readily due to the stronger *trans* effect of MeCN compared to that of iodide, leading to [RhI(COMe)(**1**)(NCMe)$_2$]$^+$, the same acetyl complex formed in route A. The released iodide ligand is recycled to generate more [RhI(**1**)(CO)] from the starting complex.

It should be noted that related replacements of I$^-$ and MeCN have been observed previously for acetylrhodium(III) complexes, for example between [RhI$_3$(COMe)(CO)(NCMe)]$^-$ and [RhI$_2$(COMe)(CO)(NCMe)$_2$].[63] In addition, in the iridium-catalysed methanol carbonylation reaction, I$^-$ is first substituted for CO in [IrI$_3$Me(CO)$_2$]$^-$ to give the neutral complex [IrI$_2$Me(CO)$_3$], before CO migratory insertion can take place.[7,63] The absence of iodide with its weak *trans* effect and a decrease of the negative charge at the metal centre facilitate the migratory insertion process.

In an attempt to prepare the final complex [RhI(COMe)(**1**)(NCMe)$_2$]SbF$_6$ by an independent route, the dimeric complex [RhI(μ-I)(COMe)(CO)(NCMe)]$_2$, previously prepared by Haynes and co-workers,[63] was treated with 2,2′-bipyridine. This resulted in the formation of a new complex [RhI$_2$(COMe)(**1**)(CO)], which was fully characterised and shows ν(CO) and ν(COMe) IR bands (in Nujol) at 2058 and 1694 cm^{-1}, respectively. Although the exact stereochemical arrangement of the ligands could not be established, an arrangement with the acetyl group *trans* to the iodido ligand is proposed, as shown in Equation (2), on the basis of the relative *trans* effects of the ligands and similarities with other acetylrhodium(III) complexes. Subsequent removal of one of the iodido ligands by the addition of 1 equiv. of AgSbF$_6$ in MeCN resulted in a complex mixture of products that could not be analysed. The addition of 2 equiv. of AgSbF$_6$ in MeCN also resulted in a complex mixture of products.

In summary, the reaction of [Rh(**1**)(CO)$_2$]SbF$_6$ with MeI in MeCN is approximately 3000 times slower than the oxidative addition of MeI to [RhI(**1**)(CO)] in CH$_2$Cl$_2$. The neutral complex [RhI(**1**)(CO)] is formed in situ by substitution of a CO ligand in [Rh(**1**)(CO)$_2$]$^+$. Oxidative additions of MeI at [Rh(**1**)(CO)$_2$]SbF$_6$ and [RhI(**1**)(CO)], therefore, occur simultaneously to yield a common acetylrhodium(III) product. This is an important insight into the potential reactivity of [Rh(**1**)(CO)$_2$]SbF$_6$ during carbonylation reactions as the presence of iodide will lead to the formation of a neutral complex [RhI(**1**)(CO)], which undergoes much more rapid oxidative addition. It is also possible that



(2)

[Rh(**1**)$(CO)_2$]SbF_6 and [RhI(**1**)(CO)] are both active species in carbonylation reactions, which are described in the next section.

Carbonylation Studies

Initial carbonylation reactions of methyl acetate were carried out by using methyl iodide as the co-catalyst in a solvent mixture of acetic acid and water (see Exp. Sect. for details). Quantitative conversion of methyl acetate to acetic acid can be achieved by using the benchmark catalyst precursor $[RhCl(CO)_2]_2$ under the conditions used (Run 2). Runs 3 and 4 show that when the amount of rhodium catalyst is lowered to 25 µmol, the conversion of methyl acetate is reduced to approximately 50%. All other catalysts have been tested under these reaction conditions (P = 30 bar, T = 130 °C, t = 16 h), and the results in Table 5 show that fairly similar conversions are obtained for all catalysts containing ligands **1**–**5** compared to $[RhCl(CO)_2]_2$. In the absence of methyl iodide, no carbonylation was observed.

Table 5. Carbonylation of methyl acetate under aqueous conditions.[a]

Run	Catalyst	Rh [µmol]	MeI [mmol]	Conv.[b] [%]	TOF [h^{-1}]
1	$[RhCl(CO)_2]_2$	58	90	73	160
2	$[RhCl(CO)_2]_2$	80	80	100	160
3	$[RhCl(CO)_2]_2$	24	80	48	250
4	$[RhCl(CO)_2]_2$	26	90	49	240
5	[Rh(**1**)$(CO)_2$]SbF_6	24	80	41	220
6	[Rh(**1**)$(CO)_2$]SbF_6	22	80	40	230
7	[Rh(**1**)$(CO)_2$]SbF_6	25	80	42	210
8	[Rh(**2**)$(CO)_2$]SbF_6	23	80	39	210
9	[Rh(**3**)$(CO)_2$]SbF_6	24	80	35	180
10	[Rh(**4**)$(CO)_2$]SbF_6	25	80	43	220
11	[Rh(**5**)$(CO)_2$]SbF_6	25	80	47	240

[a] Conditions: solvent: AcOH (0.67 mol) and H_2O (0.5 mol); substrate: MeOAc (0.2 mol); P(CO) = 30 bar; T = 130 °C, t = 16 h. [b] Conversion of methyl acetate, determined by ^1H NMR spectroscopy.

In order to avoid aqueous acidic conditions, the carbonylation of methyl acetate to acetic anhydride was investigated under anhydrous conditions by using methyl acetate as the substrate and solvent and LiI as the co-catalyst. The first three runs in Table 6 were carried out to confirm reproducibility. When the iodide concentration is halved, the TOF is approximately halved (Runs 3/4 and Runs 5/6), in line with a first-order dependence on the iodide concentration commonly observed in rhodium-based carbonylation systems.[64,65] The effect of temperature is illustrated in Runs 6–8, whereby the TOF is dramatically increased at 195 °C, which is similar to the temperatures used in industrial processes. In order to minimise catalyst decomposition, the catalytic activities of [Rh(**1**)$(CO)_2$]SbF_6 and [Rh(**3**)$(CO)_2$]SbF_6 (Runs 11–14) were determined at 130 °C. It can be seen from Runs 11–14 that under these conditions, the TOFs are somewhat lower but comparable to $[RhCl(CO)_2]_2$ (Runs 1–3).

Stability studies in acetic acid have shown that the lifetime of the complexes decreases with an increase in the size of the 6,6′-substituents at the bipyridine ligand. Furthermore, the oxidative addition experiments with MeI have shown that the presence of iodide leads to the formation of neutral complexes of the type [RhI(L)(CO)], which undergo a much faster oxidative addition reaction compared to cationic complexes. Taking all results into consideration, we conclude that under the carbonylation conditions used, in the presence of excess iodide and CO, it is very likely that all cationic complexes $[Rh(L)(CO)_2]^+$ studied here, are rapidly converted to neutral complexes of the type [RhI(L)(CO)], potentially followed by further slower substitution of the bipy ligand to give a common active species $[RhI_2(CO)_2]^-$ in all cases.

Conclusions

A series of *cis*-dicarbonylrhodium(I) complexes $[Rh(L)(CO)_2]SbF_6$ containing 6,6′-disubstituted bipyridine ligands has been synthesised. Depending on the size of the substituents, a deviation between the plane of the bipyridine ligand and the metal coordination plane is observed. Metal–metal interactions as well π–π interactions are observed in the solid-state structures of the complexes containing ligands **2**–**4**, which are thought to be responsible for additional peaks observed in the carbonyl region of the IR spectrum.

The stability of the complexes containing ligands **3**–**5** under conditions that are comparable to those during carbonylation experiments, was investigated in CD_3COOD by ^1H NMR spectroscopy. The stability decreases with the size of the substituents in the 6,6′-positions and is believed to be related to the catalytic activity observed in carbonylation experiments. Whereas the more stable complexes containing ligands **1**–**3** generally show a slightly lower activity compared to experiments with $[RhCl(CO)_2]_2$, the complexes with ligands **4** and **5** show comparable activities. Taking all these observations together, it is concluded that all complexes under the carbonylation conditions, where an excess of iodide is present, are eventually converted into the well-known carbonylation catalyst $[RhI_2(CO)_2]^-$. In the case of

Table 6. Carbonylation of methyl acetate under anhydrous conditions.[a]

Run	Catalyst	T [°C]	Rh [µmol]	LiI [mmol]	Ac_2O [g]	AcOH [g]	Conv. [%]	TOF [h^{-1}]
1	$[RhCl(CO)_2]_2$	130	42	30	1.8	0.2	4.0	29
2	$[RhCl(CO)_2]_2$	130	42	30	1.2	0.4	3.6	27
3	$[RhCl(CO)_2]_2$	130	41	30	1.3	0.3	3.2	25
4	$[RhCl(CO)_2]_2$	130	42	15	0.7	0.3	2.1	15
5	$[RhCl(CO)_2]_2$	130	78	15	1.7	0.3	4.2	17
6	$[RhCl(CO)_2]_2$	130	78	7	0.5	0.2	1.6	7
7	$[RhCl(CO)_2]_2$	150	76	15	3.1	0.6	7.7	33
8	$[RhCl(CO)_2]_2$	195	36	16	34	2.7	76	660
11	[Rh(**1**)(CO)$_2$]SbF$_6$	130	41	30	0.1	0.3	1.0	8
12	[Rh(**1**)(CO)$_2$]SbF$_6$	130	41	30	0.1	0.4	1.4	11
13	[Rh(**1**)(CO)$_2$]SbF$_6$	130	40	30	0.1	0.2	0.9	7
14	[Rh(**3**)(CO)$_2$]SbF$_6$	130	41	30	0.2	0.3	1.3	10

[a] Conditions: substrate: MeOAc (0.51 mol); P(CO) = 40 bar; t = 16 h.

the less stable complexes [Rh(**4**)(CO)$_2$]$^+$ and [Rh(**5**)(CO)$_2$]$^+$, substitution of the bipy ligands with iodido ligands is probably faster, resulting in similar activities being observed for these complexes compared to $[RhI_2(CO)_2]^-$, whereas for the complexes containing ligands **1**–**3**, the slower substitution of these bipy ligands results in a reduced overall catalytic activity. The bipyridine ligands **1**–**3** appear to retard the carbonylation reaction and are therefore not suited for application in carbonylation catalysis. A possible reason why the cationic dicarbonylrhodium(I) complexes are less active than $[RhI_2(CO)_2]^-$, is the lower electron density at the rhodium(I) centre, which reduces the rate of oxidative addition of MeI. Reactivity studies of [Rh(**1**)(CO)$_2$]$^+$ with MeI in acetonitrile have shown that oxidative addition does occur, but is much slower than the oxidative addition at the neutral complex [RhI(**1**)(CO)], which is formed during the reaction. Further substitution to remove the bipyridine ligands and form the anionic complex $[RhI_2(CO)_2]^-$ was not observed under these reaction conditions, but cannot be excluded at this stage. These results raise an important question regarding the general applicability of ligand-substituted rhodium complexes in carbonylation catalysis, and further studies will be needed to clarify this.

Experimental Section

General Remarks: All moisture- and oxygen-sensitive compounds were prepared by using standard high-vacuum line, Schlenk and cannula techniques. A standard nitrogen-filled glove box was used for any subsequent manipulation and storage of these compounds. Standard ^1H, ^{19}F, ^{31}P and ^{13}C NMR spectra were recorded with a Bruker AV-400 or DRX-400 spectrometer. ^1H NMR spectra were referenced to the residual nondeuterated solvent signal and ^{13}C NMR chemical shifts to the signal of the deuterated solvent. The ^{31}P NMR chemical shifts were referenced to H_3PO_4. The ^{19}F NMR chemical shifts were referenced to $CFCl_3$. Mass spectra were recorded with either a VG Autospec or a VG Platform II spectrometer. IR measurements were carried out with a Perkin–Elmer Spectrum RX or GX FT-IR spectrometer. In situ IR measurements were performed with a thermostatted solution cell (CaF_2 windows, 0.5 mm path length) as described previously.[38] Elemental analyses were performed by the Science Technical Support Unit at The London Metropolitan University. CCDC-748277 {for [Rh(**3**)(CO)$_2$]SbF$_6$} and CCDC-748278 {for [Rh(**4**)(CO)$_2$]SbF$_6$} 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.

Solvents and Reagents: Diethyl ether and tetrahydrofuran were dried by prolonged reflux under nitrogen in the presence of sodium metal with a benzophenone ketyl indicator and distilled freshly prior to use. Dichloromethane and acetonitrile were treated in a similar manner, but by using calcium hydride as the drying agent. Toluene and pentane were dried by passing through a column, packed with commercially available Q-5 reagent (13 % CuO on alumina) and activated alumina (pellets, 3 mm), in a stream of nitrogen. Methyl acetate was dried with P_2O_5 and distilled under nitrogen. Acetone was dried with B_2O_3 and distilled under nitrogen. The starting materials $[RhCl(CO)_2]_2$,[66] $[RhCl(cod)]_2$,[67] $[RhI_2(COMe)(CO)(MeCN)]_2$,[63] 2,2′-dipyridone,[68] and the ligands 6,6′-diamino-2,2′-bipyridine (**2**)[42] and diethyl 2,2′-bipyridine-6,6′-bis(phosphonate) (**5**)[69] were prepared according to published procedures. The preparation of diethyl 2,2′-bipyridine-6,6′-bis(carboxylate) (**4**) was adapted from a previously published procedure.[70]

Synthesis of Ligands

Diethyl 2,2′-Bipyridine-6,6′-bis(carboxylate) (4): A 300 mL high-pressure reactor was charged with $[PdCl_2(PPh_3)_2]$ (90 mg, 0.13 mmol), 6,6′-dibromo-2,2′-bipyridine (1 g, 3.19 mmol), NEt_3 (15 mL), ethanol (15 mL) and CO (10 bar). The reactor was heated to 80 °C for 24 h before cooling to room temperature and venting the CO. The resultant black suspension was pumped to dryness before adding dichloromethane (50 mL) and filtering through a silica pad to afford an orange solution. The dichloromethane was removed in vacuo and the product (0.68 g, 61 %) purified on an Et_3N-deactivated silica column with a 90:10 hexane/dichloromethane solvent system. $C_{16}H_{16}N_2O_4$ (300.31): calcd. C 63.99, H 5.37, N 9.33; found C 64.05, H 5.34, N 9.38. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.77 (d, ^3J = 7.6 Hz, 2 H, Ar-H), 8.16 (d, ^3J = 7.6 Hz, 2 H, Ar-H), 7.99 (t, ^3J = 7.6 Hz, 2 H, Ar-H), 4.5 (q, ^3J = 7.1 Hz, 4 H, CH_2), 1.48 (t, ^3J = 7.1 Hz, 6 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR [101 MHz, $(CD_3)_2CO$]: δ = 15.6 (CH_3), 63.1 (CH_2), 125.7, 127.13, 140.27, 150.1 (Ar C_{ipso}), 157.1 (Ar C_{ipso}), 166.5 (CO_2Et) ppm. IR (nujol): $\tilde{\nu}$ = 1733 (CO) cm^{-1}. ESI/MS$^+$: m/z (%) = 323 [M + Na]$^+$, 100, 301 (48) [M + H]$^+$.

6,6′-Bis(*tert*-butyldimethylsiloxy)-2,2′-bipyridine: A 50 mL, two-neck round-bottomed flask was loaded with 2,2′-bipyridone (0.78 g, 4.14 mmol), *tert*-butyldimethylsilyl chloride (2.5 g, 16.6 mmol), a stirrer bar, fitted with a reflux condenser, and nitrogen was introduced to the system. Dry triethylamine was added with stirring during which time a grey emulsion formed. The mixture was subsequently refluxed overnight. The resulting suspension was filtered under reduced pressure and the remaining solid washed with a further 10 mL of triethylamine after which the solvent was removed under reduced pressure. The resulting beige solid was dissolved in hot methanol, allowed to cool to room temp. and then cooled to –20 °C to induce crystallisation. The white solid was rapidly filtered and washed with two portions of cold methanol, dried under vacuum, and stored in a glove box. Yield: 0.54 g (31%). $C_{22}H_{36}N_2O_2Si_2$ (416.71): calcd. C 63.41, H 8.71, N 6.72; found C 63.50, H 8.82, N 6.79. ^{1}H NMR (CD_2Cl_2): δ = 0.42 [s, 12 H, Si(CH_3)$_2$], 1.03 [s, 18 H, SiC(CH_3)$_3$], 6.71 (dd, J = 0.8, 8.1 Hz, 2 H, Ar-H), 7.69 (t, J = 7.8 Hz, 2 H Ar-H), 7.92 (dd, J = 0.8, 7.5 Hz, 2 H, Ar-H) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = –4.5, 17.9, 25.6, 112.9, 113.6, 139.8, 153.7, 162.2 ppm. MS [CI]: *m/z* (%) = 417 (100) [M + H]$^+$.

Synthesis of Metal Complexes

[Rh(1)(CO)$_2$]SbF$_6$: $AgSbF_6$ (0.280 g, 0.82 mmol) was dissolved in acetone (10 mL) and added to [RhCl(cod)]$_2$ (0.204 g, 0.41 mmol) to form a yellow solution and a white precipitate. The suspension was stirred for 15 min before filtering. The filtrate was added to 2,2′-bipyridine (**1**; 0.127 g, 0.82 mmol) dissolved in acetone (5 mL). The resultant orange solution was stirred for 20 min before removing the solvent in vacuo and re-dissolving in dichloromethane (5 mL). CO was then bubbled through the solution for 30 min to afford the product as a green precipitate (0.36 g, 80%), which was isolated by filtration, washed with dichloromethane (2 × 3 mL portions) and dried in vacuo. $C_{12}H_8F_6N_2O_2RhSb$ (550.85): calcd. C 26.17, H 1.46, N 5.09; found C 26.25, H 1.49, N 5.04. ^{1}H NMR [400 MHz, $(CD_3)_2CO$]: δ = 9.07 (d, ^3J = 5.7 Hz, 2 H, Ar-H), 8.74 (d, ^3J = 7.8 Hz, 2 H, Ar-H), 8.54 (td, ^3J = 7.9, ^4J = 1.2 Hz, 2 H, Ar-H), 7.97 (ddd, ^3J = 7.9, ^3J = 5.7, ^4J = 1.5 Hz, 2 H, Ar-H) ppm. ^{13}C{^{1}H} NMR [101 MHz, $(CD_3)_2CO$]: δ = 125.2, 129.6, 143.8, 156.0, 157.4 (Ar C_{ipso}), 184.3 (d, $^1J_{\text{C-Rh}}$ = 69.5 Hz, Rh-CO) ppm. ^{19}F NMR [377 MHz, $(CD_3)_2CO$]: δ = –122.2 (superposition of sext due to $^{121}SbF_6^-$ and oct due to $^{123}SbF_6^-$) ppm. IR (nujol): $\tilde{\nu}$ = 2109, 2054 (CO) cm^{-1}. FAB/MS$^+$: *m/z* (%) = 315 (100) [M]$^+$. FAB/MS$^-$: *m/z* (%) = 235 (100) [M]$^-$.

[Rh(2)(cod)]SbF$_6$: $AgSbF_6$ (0.131 g, 0.38 mmol) was dissolved in acetone (10 mL) and added to [RhCl(cod)]$_2$ (0.094 g, 0.19 mmol) to form a light yellow solution and a white precipitate. The suspension was stirred for 20 min before filtering. The filtrate was added to 6,6′-bis(*tert*-butyldimethylsilyloxy)-2,2′-bipyridine (0.158 g, 0.38 mmol) dissolved in deoxygenated technical grade acetone (30 mL). The resultant dark orange solution was stirred for 30 min before concentrating (ca. 2 mL) and adding pentane (30 mL) to afford the product as a yellow solid (0.246 g, 75%). The solid was isolated by filtration, washed with pentane (2 × 3 mL portions), and dried in vacuo. $C_{18}H_{20}F_6N_2O_2RhSb$ (635.01): calcd. C 34.05, H 3.17, N 4.41; found C 33.97, H 3.20, N 4.35. ^{1}H NMR [400 MHz, $(CD_3)_2CO$]: δ = 11.58 (br., OH), 8.02 (t, ^3J = 7.9 Hz, 2 H, Ar-H), 7.92 (d, ^3J = 7.9 Hz, 2 H, Ar-H), 7.05 (d, ^3J = 7.9 Hz, 2 H, Ar-H), 5.34 (br., 4 H, CH), 2.39 (m, 4 H, CH_2), 1.89 (q, ^3J = 8.2 Hz, 4 H, CH_2) ppm. ^{13}C{^{1}H} NMR [101 MHz, $(CD_3)_2CO$]: δ = 168.5 (Ar C_{ipso}), 156.8 (Ar C_{ipso}), 144.8, 117.3, 115.3, 85.0 (d, $^1J_{\text{C-Rh}}$ = 12.5 Hz, Rh-CH), 32.2 (CH$_2$) ppm. ^{19}F NMR [377 MHz, $(CD_3)_2CO$]: δ = –123.4 (superposition of sext due to $^{121}SbF_6^-$ and oct due to $^{123}SbF_6^-$) ppm. IR (nujol): $\tilde{\nu}$ = 3375 (OH) cm^{-1}. FAB/MS$^+$: *m/z* (%) = 399 (100) [M]$^+$. FAB/MS$^-$: *m/z* (%) = 235 (100) [M]$^-$.

[Rh(2)(CO)$_2$]SbF$_6$: $AgSbF_6$ (0.118 g, 0.344 mmol) was dissolved in acetone (10 mL) and added to [RhCl(cod)]$_2$ (0.085 g, 0.172 mmol) to form a light yellow solution and a white precipitate. The suspension was stirred for 20 min before filtering. The filtrate was added to 6,6′-bis(*tert*-butyldimethylsilyloxy)-2,2′-bipyridine (0.144 g, 0.344 mmol) dissolved in deoxygenated technical grade acetone (30 mL). The resultant dark orange solution was stirred for 30 min before concentrating (ca. 2 mL) and adding pentane (30 mL) to afford a yellow precipitate, which was isolated by filtration. The yellow precipitate was dissolved in dichloromethane (15 mL), and CO was bubbled through the solution for 30 min whilst stirring. The solution was reduced to 2 mL before adding pentane (30 mL) to afford the product as a green precipitate (0.162 g, 81%). The solid was isolated by filtration, washed with pentane (2 × 5 mL portions), and dried in vacuo. $C_{12}H_8F_6N_2O_4RhSb$ (582.85): calcd. C 24.73, H 1.38, N 4.81; found C 24.82, H 1.43, N 4.74. ^{1}H NMR [400 MHz, $(CD_3)_2CO$]: δ = 12.87 (br., OH), 8.17 (t, ^3J = 8.0 Hz, 2 H, Ar-H), 7.96 (d, ^3J = 8.0 Hz, 2 H, Ar-H), 7.30 (d, ^3J = 8.0 Hz, 2 H, Ar-H) ppm. ^{13}C{^{1}H} NMR [101 MHz, $(CD_3)_2CO$]: δ = 114.4, 116.8, 145.8, 155.6 (Ar C_{ipso}), 164.4 (Ar C_{ipso}), 184.3 (d, $^1J_{\text{C-Rh}}$ = 70.9 Hz, Rh-CO) ppm. ^{19}F NMR [377 MHz, $(CD_3)_2CO$]: δ = –123.0 (superposition of sext due to $^{121}SbF_6^-$ and oct due to $^{123}SbF_6^-$) ppm. IR (nujol): $\tilde{\nu}$ = 3324 (OH); 2108, 2052 (CO) cm^{-1}. FAB/MS$^+$: *m/z* (%) = 347 (100) [M]$^+$. FAB/MS$^-$: *m/z* (%) = 235 (100) [M]$^-$.

[Rh(3)(CO)$_2$]SbF$_6$: $AgSbF_6$ (0.213 g, 0.61 mmol) was dissolved in acetone (15 mL) and added to [RhCl(cod)]$_2$ (0.153 g, 0.31 mmol) to form a yellow solution and a white precipitate. The suspension was stirred for 15 min before filtering. The filtrate was added to 6,6′-diamino-2,2′-bipyridine (**3**; 0.116 g, 0.61 mmol) dissolved in acetone (5 mL). The resultant solution was stirred for 20 min before removing the solvent in vacuo and re-dissolving the resultant orange solid in dichloromethane (15 mL). CO was bubbled through the orange/brown suspension for 30 min whilst stirring. The dichloromethane suspension was concentrated (ca. 2 mL) before adding diethyl ether (30 mL) to afford the product as a brown precipitate (0.251 g, 73%). The solid was isolated by filtration and washed with diethyl ether (2 × 3 mL portions) before drying in vacuo. $C_{12}H_{10}F_6N_4O_2RhSb$ (580.88): calcd. C 24.81, H 1.74, N 9.65; found C 24.95, H 1.79, N 9.56. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.81 (t, ^3J = 7.9 Hz, 2 H, Ar-H), 7.43 (d, ^3J = 7.9 Hz, 2 H, Ar-H), 6.9 (d, ^3J = 7.9 Hz, 2 H, Ar-H), 5.52 (br., 4 H, NH_2) ppm. ^{13}C{^{1}H} NMR [101 MHz, $(CD_3)_2CO$]: δ = 112.1, 113.3, 141.6, 153.3 (Ar C_{ipso}), 161.4 (Ar C_{ipso}), 183.3 (d, $^1J_{\text{C-Rh}}$ = 69.1 Hz, Rh-CO) ppm. ^{19}F NMR [377 MHz, $(CD_3)_2CO$]: δ = –123.4 (superposition of sext due to $^{121}SbF_6^-$ and oct due to $^{123}SbF_6^-$) ppm. IR (nujol): $\tilde{\nu}$ = 3473, 3378 (NH$_2$); 2097, 2035 (CO) cm^{-1}. FAB/MS$^+$: *mz* (%) = 345 (100) [M]$^+$. FAB/MS$^-$: *m/z* (%) = 235 (100) [M]$^-$.

Crystal Data for [Rh(3)(CO)$_2$]SbF$_6$: [$C_{12}H_{10}N_4O_2Rh$]SbF$_6$, M = 580.90, monoclinic, *I*2/*a* (no. 15), a = 12.96970(18), b = 12.62358(16), c = 20.7263(3) Å, β = 93.0730(11)°, V = 3388.51(8) Å^3, Z = 8, $D_{\text{calcd.}}$ = 2.277 g cm^{-3}, μ(Mo-K_α) = 2.646 mm^{-1}, T = 173 K, yellow blocks, Oxford Diffraction Xcalibur 3 diffractometer; 5653 independent measured reflections (R_{int} = 0.0302), F^2 refinement, R_1(obs.) = 0.0210, wR_2(all) = 0.0543, 5321 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{\max}$ = 65°], 252 parameters.

[Rh(4)(CO)$_2$]SbF$_6$: $AgSbF_6$ (0.115 g, 0.333 mmol) was dissolved in acetone (10 mL) and added to [RhCl(cod)]$_2$ (0.082 g, 0.0.167 mmol) to form a yellow solution and a white precipitate. The suspension was stirred for 15 min before filtering. The filtrate was added to diethyl 2,2′-bipyridine-6,6′-biscarboxylate) (**4**; 0.1 g, 0.333 mmol) dissolved in acetone (5 mL) and stirred for 20 min before removing the solvent. The resultant solid was dissolved in dichloromethane (15 mL) before bubbling CO through the solution for 2.5 h whilst stirring to give an orange/brown suspension. Pentane (30 mL) was added to the suspension to yield the product as an orange solid (0.178 g, 77%), which was isolated by filtration and dried in vacuo. $C_{18}H_{16}F_6N_2O_6RhSb$ (694.98): calcd. C 31.11, H 2.32, N 4.03; found C 30.99, H 2.25, N 3.93. ^{1}H NMR [400 MHz, $(CD_3)_2CO$]: δ = 9.06 (d, ^3J = 7.8 Hz, 2 H, Ar-*H*), 8.75 (t, ^3J = 7.8 Hz, 2 H, Ar-*H*), 8.57 (d, ^3J = 7.8 Hz, 2 H, Ar-*H*), 4.63 (q, ^3J = 7.1 Hz, 4 H, CH_2), 1.51 (t, ^3J = 7.1 Hz, 6 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR [101 MHz, $(CD_3)_2CO$]: δ = 14.4 (C-CH_3), 64.9 (C-CH_2), 128.5, 129.9, 145.1, 152.3 (Ar C_{ipso}), 157.7 (Ar C_{ipso}), 165.3 (CO_2Et), 182.4 (d, $^1J_{C\text{-}Rh}$ = 60.0 Hz, Rh-*C*O) ppm. ^{19}F NMR [377 MHz, $(CD_3)_2CO$]: δ = –123.3 (superposition of sext due to $^{121}SbF_6^-$ and oct due to $^{123}SbF_6^-$) ppm. IR (nujol): ṽ = 2097, 2041 (CO); 1722 (CO) cm^{-1}. FAB/MS$^+$: *m/z* (%) = 403 (100) [M – 2 CO]$^+$, 459 (8) [M]$^+$. FAB/MS$^-$: *m/z* (%) = 235 (100) [M]$^-$.

Crystal Data for $[Rh(4)(CO)_2]SbF_6$: $[C_{18}H_{16}N_2O_6Rh](SbF_6)$, *M* = 694.99, orthorhombic, $Pna2_1$ (no. 33), *a* = 15.66829(19), *b* = 15.58784(16), *c* = 18.44328(18) Å, *V* = 4504.49(8) Å^3, *Z* = 8 (two independent complexes), $D_{calcd.}$ = 2.050 g cm^{-3}, $\mu(Cu\text{-}K_\alpha)$ = 16.266 mm^{-1}, *T* = 173 K, yellow needles, Oxford Diffraction Xcalibur PX Ultra diffractometer; 8682 independent measured reflections (R_{int} = 0.0510), F^2 refinement, R_1(obs.) = 0.0315, wR_2(all) = 0.0873, 7051 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 143°], 633 parameters. The absolute structure was shown to be a polar twin by a combination of *R*-factor tests (R_1^+ = 0.0359, R_1^- = 0.0363) and by use of the Flack parameter [x^+ = +0.490(8), x^- = +0.510(8)].

$[Rh(5)(CO)_2]SbF_6$: $AgSbF_6$ (0.080 g, 0.234 mmol) was dissolved in acetone (10 mL) and added to $[RhCl(cod)]_2$ (0.058 g, 0.117 mmol) to form a yellow solution and a white precipitate. The suspension was stirred for 15 min before filtering. The filtrate was added to diethyl 2,2′-bipyridine-6,6′-bis(phosphonate) (**5**; 0.1 g, 0.234 mmol) dissolved in dry acetone (5 mL) whilst stirring. After 20 min, the volatiles were removed before adding toluene (25 mL) to afford a brown solid suspension in a yellow solution. CO was bubbled through the suspension for 30 min whilst stirring. The suspension was then heated at 80 °C under CO for 5 h. The product was isolated as a green solid (0.124 g, 49%) by filtration before washing with toluene (2 × 5 mL) and drying in vacuo. $C_{20}H_{26}F_6N_2O_8RhSb$ (761.08): calcd. C 29.19, H 3.18, N 3.4; found C 26.18, H 3.09, N 3.13. ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ = 8.91 (d, ^3J = 7.7 Hz, 2 H), 8.60 (td, $^3J_{HH}$ = 7.7, $^3J_{HP}$ = 4.4 Hz, 2 H), 8.36 (t, ^3J = 7.7 Hz, 2 H), 4.36 (m, 8 H, CH_2), 1.41 (t, ^3J = 7.1 Hz, 12 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $(CD_3)_2CO$): δ = 16.7 (C-CH_3), 65.0 (C-CH_2), 127.0, 131.6 (d, $^2J_{C\text{-}P}$ = 18.3 Hz, Ar *C*), 142.5, 154.6 (d, $^1J_{C\text{-}P}$ = 237.9 Hz, Ar *C*-P), 157.2 (Ar C_{ipso}), 181.4 (d, $^1J_{C\text{-}Rh}$ = 73.4 Hz, Rh-*C*O) ppm. ^{31}P NMR [162 MHz, $(CD_3)_2CO$]: δ = 9.58 ppm. ^{19}F NMR (377 MHz, $(CD_3)_2CO$): δ = –123.4 (superposition of sext due to $^{121}SbF_6^-$ and oct due to $^{123}SbF_6^-$) ppm. IR (nujol): ṽ = 2096, 2033 (CO) cm^{-1}. FAB/MS$^+$: *mz* (%) = 531 (100) [M – 2 CO]$^+$. FAB/MS$^-$: *m/z* (%) = 235 (100) [M]$^-$.

$[RhI_2(COMe)(CO)(bipy)]$: The dimeric complex $[RhI_2(COMe)(CO)(MeCN)]_2$ (140 mg, 0.149 mmol) was dissolved in dichloromethane (20 mL) and transferred to a stirred solution of 2,2′-bipyridine (47 mg, 0.298 mmol) dissolved in dichloromethane (5 mL). The resultant solution was heated at reflux for 1 h before cooling to room temperature and reducing the volume of solvent to 2 mL. Pentane (30 mL) was added to yield the product as an orange precipitate (152 mg, 86%), which was isolated by filtration and dried in vacuo. $C_{13}H_{11}I_2N_2O_2Rh$ (583.96): calcd. C 26.74, H 1.9, N 4.8; found C 26.84, H 1.5, N 4.76. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.03 (d, ^3J = 5.7 Hz, 1 H, Ar-H_{ortho}), 8.96 (d, ^3J = 5.1 Hz, 1 H, Ar-H_{ortho}), 8.18 (t, ^3J = 7.8 Hz, 2 H, Ar-H_{meta}), d 8.04 (m, 2 H, Ar-H_{para}), 7.67 (m, 1 H, Ar-H_{meta}), 7.58 (m, 1 H, Ar-H_{meta}), 3.16 (s, 3 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 217.8 (d, $^1J_{C\text{-}Rh}$ = 18.6 Hz, Rh-*C*OMe), 185.3 (d, $^1J_{C\text{-}Rh}$ = 62.1 Hz, Rh-*C*O), 155.3 (Ar-C_{ipso}), 153.8 (Ar-C_{ortho}), 153.3 (Ar-C_{ipso}), 151.0 (Ar-C_{ortho}), 139.7 (Ar-C_{para}), 139.2 (Ar-C_{para}), 126.7 (Ar-C_{meta}), 126.6 (Ar-C_{meta}), 123.0 (Ar-C_{meta}), 123.0 (Ar-C_{meta}), 52.8 (s, CH_3) ppm. IR (nujol): ṽ = 2058 (CO), 1694 (COMe) cm^{-1}. ESI/MS$^+$: *m/z* (%) = 457 (100) [M – I]$^+$.

Methyl Acetate Carbonylation with MeI: A 300 mL high-pressure reactor was charged with AcOH (40 g, 0.67 mol), MeOAc (15 g, 0.2 mol), H_2O (9 g, 0.5 mol), MeI (10.5 g, 74 mmol), a rhodium compound (25 μmol) and CO (30 bar) before heating at 130 °C for 16 h. After cooling the reactor to 5 °C, the CO was vented from the reactor and the reaction mixture weighed. A 150 mg aliquot of the reaction mixture was weighed into a vial with MeCN (50 mg) before mixing and analysing by ^{1}H NMR spectroscopy in [D$_6$]-DMSO. The molar composition of the reaction mixture was determined by integration of the ^{1}H NMR peaks relative to the MeCN standard (see Figure S10). Carbonylation reactions without methyl iodide as the co-catalyst were carried out in a similar way, except that more MeOAc was used (21 g, 0.28 mol).

Methyl Acetate Carbonylation with LiI: A rhodium compound (42 μmol) and LiI (4 g, 30 mmol) were dissolved in anhydrous MeOAc (38 g, 0.51 mol) before transferring to a nitrogen-purged 300 mL high-pressure reactor. The reactor was then pressurised with CO (40 bar) and heated at 130 °C for 16 h. After cooling the reactor to 5 °C, the CO was vented from the reactor, and the reaction mixture was weighed. A 150 mg aliquot of the reaction mixture was weighed into a vial with MeCN (50 mg) before mixing and analysing by ^{1}H NMR spectroscopy in $(CD_3)_2SO$. The molar composition of the reaction mixture was determined by integration of the ^{1}H NMR peaks relative to the MeCN standard (see Figure S11). Carbonylation reactions without the iodide co-catalysts were carried out in exactly the same way, but without LiI.

Supporting Information (see footnote on the first page of this article): Selected NMR and IR spectra of the complexes and NMR spectra of the carbonylation product analysis and stability measurements, as well as crystallographic details for complexes $[Rh(3)(CO)_2]SbF_6$ and $[Rh(4)(CO)_2]SbF_6$.

Acknowledgments

We are grateful to BP Chemicals Ltd and Engineering & Physical Sciences Research Council (EPSRC) for financial support. We thank Johnson Matthey for their generous loan of $RhCl_3$.

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Received: April 19, 2011