[12] Authentic samples of *anti*-diols were prepared as follows: 1) α-Hydroxyketones (R^{1}CHOHCOR^2) were prepared following the Kagan SmI$_2$ coupling (J. Souppe, J.-L. Namy, H. B. Kagan, *Tetrahedron Lett.* **1984**, *25*, 2869–2872); 2) protection of the hydroxy group as tetrahydropyranyl or benzyl ether; 3) stereoselective addition of a vinyl Grignard reagent (W. C. Still, J. H. McDonald III, *Tetrahedron Lett.* **1980**, *21*, 1031–1034). The stereochemistry of the diols was also confirmed by NOE experiments on the corresponding acetonides.

[13] For catalytic pinacol coupling reactions using manganese or zinc as reductants, see: A. Gansäuer, D. Bauer, *J. Org. Chem.* **1998**, *63*, 2070–2071; A. Gansäuer, M. Moschioni, D. Bauer, *Eur. J. Org. Chem.* **1998**, 1923–1927; M. S. Dunlap, K. M. Nicholas, *Synth. Commun.* **1999**, *29*, 1097–1106; M. Bandini, P. G. Cozzi, P. Melchiorre, A. Umani-Ronchi, *Angew. Chem.* **1999**, *111*, 3558–3561; *Angew. Chem. Int. Ed.* **1999**, *38*, 3357–3359; M. Bandini, P. G. Cozzi, S. Morganti, A. Umani-Ronchi, *Tetrahedron Lett.* **1999**, *40*, 1997; U. Groth, M. Jeske, *Angew. Chem.* **2000**, *112*, 586–588; *Angew. Chem. Int. Ed.* **2000**, *39*, 574–576.

[14] a) It is known that there is a fast equilibrium between (*E*)- and (*Z*)-crotylchromium: C. T. Buse, C. H. Heathcock, *Tetrahedron Lett.* **1978**, 1685–1688; T. Hiyama, K. Kimura, H. Nozaki, *Tetrahedron Lett.* **1981**, *22*, 1037–1040; b) however, the equilibrium becomes very slow in the case of γ,γ-dialkyl-substituted allylic chromium compounds: C. Jubert, S. Nowotny, D. Kornemann, I. Antes, C. E. Tucker, P. Knochel, *J. Org. Chem.* **1992**, *57*, 6384–6386; S. Nowotny, C. E. Tucker, C. Jubert, P. Knochel, *J. Org. Chem.* **1995**, *60*, 2762–2772.

[15] There was no equilibrium between *anti*- and *syn*-diols through a retro addition of the allylic chromium species.[16] This was confirmed by the following experiment: a mixture of adducts produced at 0 °C (*anti*/*syn* = 93/7) was heated at 75 °C for 30 min before quenching; the *anti*/*syn* ratio did not change.

[16] F. Barbot, P. Miginiac, *Tetrahedron Lett.* **1975**, 3829–3832; J. Nokami, K. Yoshizane, H. Matsuura, S.-i. Sumida, *J. Am. Chem. Soc.* **1998**, *120*, 6609–6610; P. Jones, N. Millot, P. Knochel, *Chem. Commun.* **1998**, 2405–2406.

[17] To examine the equilibrium between the *cis* and *trans* allylic chromium species **9** and **10**, the following experiment was conducted: two reaction mixtures containing the enone **7**, CrCl$_2$, and Et$_3$SiCl were heated at 75 °C for 5 min. Nonanal was added at 75 °C to one mixture and stirred at the same temperature. The other mixture was cooled to 0 °C before the addition of nonanal, followed by stirring at 0 °C. The *anti*/*syn* ratio of the reaction at 75 °C was 10:90. The reaction cooled to 0 °C gave a ratio of 93:7, which is the same ratio obtained when the reaction temperature is held constant at 0 °C (Table 1). The yield of **8** in the latter reaction decreased to 39 % owing to the formation of 1,10-diphenyldecane-3,8-dione in 27 % yield, and nonanal was recovered in 45 % yield.

[18] Coordination of a siloxy group in **9** possibly stabilizes the *cis* configuration, leading to an *anti* adduct. However, the siloxy group is bulky and this could push the equilibrium to the sterically less congested *trans* isomer **10**. At higher temperatures, this steric effect could be enhanced and the proportion of the *syn* isomer increased. One possibility is that the *anti*/*syn* ratios could reflect the *cis*/*trans* ratios, which depend on a balance between these factors.

[19] For the temperature dependence of reaction rates, see: J. Otera, K. Sato, T. Tsukamoto, A. Orita, *Tetrahedron Lett.* **1998**, *39*, 3201–3204; T. Sakai, I. Kawabata, T. Kishimoto, T. Ema, M. Utaka, *J. Org. Chem.* **1997**, *62*, 4906–4907.

[20] The following functional substrates were recovered under the standard reaction conditions (Table 2, entry 1, 0 °C) owing to the mild nucleophilicity of the organochromium reagent: 1-dodecene (94 %), 1-dodecyne (98 %), 1-chlorododecane (98 %), ethyl octanoate (96 %), nonanenitrile (96 %), 4-phenyl-2-butanone (91 %), 3-phenylpropyl acrylate (87 %), and nonanal diethylene acetal (98 %).

Ligand-Controlled Chemoselectivity in the Classical Oxidative Addition Reactions of MeI and Aldehydes to Rhodium(I) Complexes**

Roman Goikhman and David Milstein*

Rhodium(I) phosphane complexes are widely used in industrial and laboratory processes owing to their catalytic properties and high reactivities, particularly in oxidative addition reactions.[1a] We report here a remarkable difference in the reactivity of similar alkylphosphanerhodium(I) complexes bearing triflate and chloride ligands in classical oxidative addition reactions of aldehydes and MeI. High chemoselectivity in oxidative addition can be achieved by the choice of complex.

[(iPr$_3$P)$_2$RhOTf] (**1**) (OTf = OSO$_2$CF$_3$, triflate) was synthesized by a simple procedure involving chloride abstraction from [{(iPr$_3$P)$_2$RhCl}$_2$] (**2**)[2] with Me$_3$SiOTf, according to our reported method;[3] an alternative synthesis has also been described.[4] Complex **1** was characterized by X-ray structure analysis, which confirmed that the geometry around the metal is square planar, and that an η^2-bound triflate ligand is present (Figure 1).[5] The structure is similar to that of another rhodium η^2-triflate complex.[4] Surprisingly, η^2 coordination of the triflate ligand in mononuclear late transition metal complexes was not reported until 1998, and the reactivity of these uncommon complexes has yet to be examined.[4, 6]

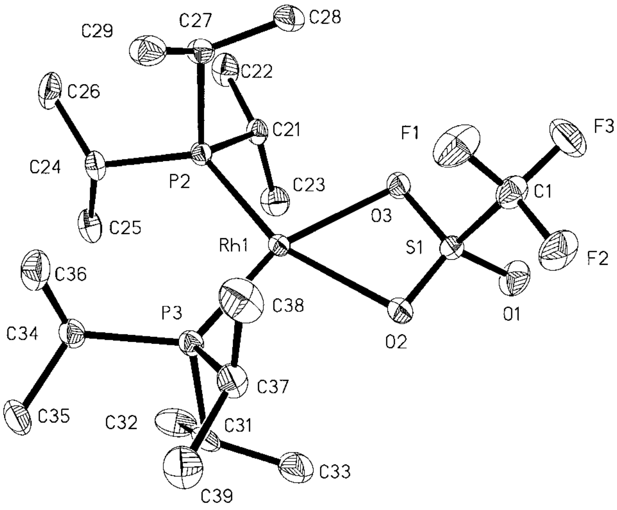

Figure 1. Structure of **1** (ORTEP plot; hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Rh1-O3 2.283(2), Rh1-O2 2.265(3), Rh1-P3 2.2099(11), Rh1-P2 2.2143(11); P3-Rh1-P2 105.41(4), P3-Rh1-O2 95.78(7), P2-Rh1-O2 158.82(7), P2-Rh1-O3 95.38(7), P3-Rh1-O3 158.96(7), O2-Rh1-O3 63.48(9).

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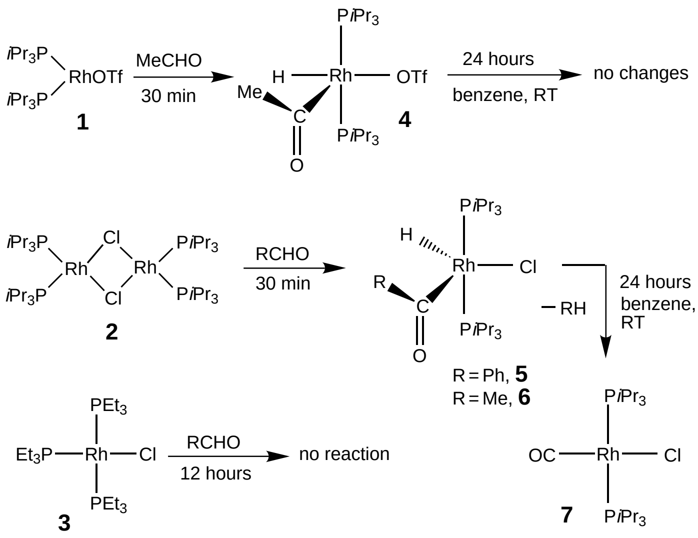
We studied the oxidative addition reactions of **1** to probe the influence of the η^2-bound triflate ligand on the reactivity of Rh^I compared to common chloro complexes such as **2** and $[(Et_3P)_3RhCl]$ (**3**).[7] The oxidative addition of aldehydes to rhodium(I) is an important reaction which plays a key role in catalytic processes such as the decarbonylation of aldehydes and hydroacylation of olefins.[1a] However, examples of acylrhodium–hydride complexes resulting from the addition of simple aldehydes to Rh^I centers are rare,[8–11] particularly because of the tendency of these complexes to undergo decarbonylation.[1b]



Scheme 1. Reactions of Rh^I complexes with aldehydes.

The oxidative addition of acetaldehyde to **1** results in the quantitative formation of the new acylrhodium–hydride complex **4** (Scheme 1).[12] X-ray structure analysis of **4** shows a square-pyramidal geometry in which the acyl ligand adopts the apical position (Figure 2).[5] Interestingly, the close analogue of **4**, namely compound **5** (Scheme 1), was reported to have a trigonal-bipyramidal structure.[11] The H-Rh-OTf angle of **4** is 169° and the MeC(O)-Rh-OTf angle is 103°, whereas the H-Rh-Cl and PhC(O)-Rh-Cl angles of **5** are 128° and 147°, respectively. It is worth noting that the Rh–H bond in **4** (1.46 Å), located *trans* to the triflate ligand, is much shorter than that in **5** (1.77 Å).

Based on theoretical calculations, it was proposed that in d^6 ML_5 complexes, a π-donating chloride ligand (e.g. the chloride of **5**) causes an orbital orientation towards a trigonal-bipyramidal structure.[11, 13] In the case of **4**, the triflate ion apparently has a negligible π-donating effect. The different structures of the closely related compounds **4** and **5** support the significant influence of π donation on the configuration of unsaturated Rh^{III} complexes.

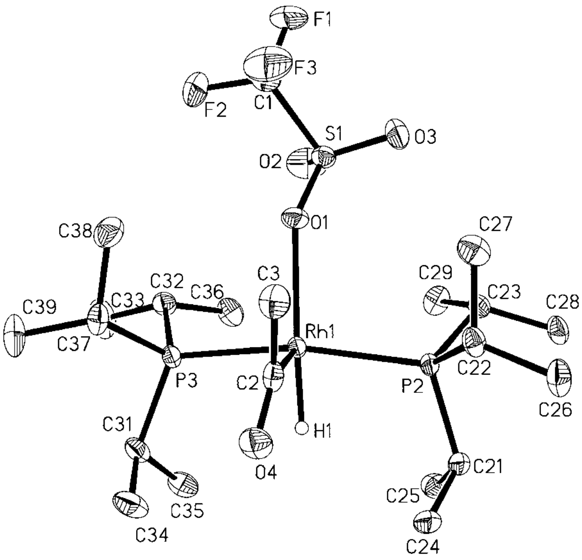


Figure 2. Structure of **4** (ORTEP plot; hydrogen atoms, except H1, are omitted for clarity). Selected bond lengths [Å] and angles [°]: Rh1-C2 1.949(2), Rh1-O1 2.2986(15), Rh1-P3 2.3428(7), Rh1-P2 2.3712(7), Rh1-H1 1.46(2); C2-Rh1-O1 103.64(8), C2-Rh1-P3 91.40(6), O1-Rh1-P3 93.31(5), C2-Rh1-P2 94.10(6), O1-Rh1-P2 98.17(5), P3-Rh1-P2 165.73(2), C2-Rh1-H1 87.3(9), P2-Rh1-H1 80.5(9), P3-Rh1-H1 86.6(9), O1-Rh1-H1 169.1(9).

The difference in the configurations of **4** and **5** is reflected in their reactivities. Whereas complex **5** and the analogous acetaldehyde adduct **6**[12, 14] undergo decarbonylation at room temperature within a few hours, giving the carbonyl complex **7** as the main product,[11, 15] complex **4** remains unchanged in benzene solution after 24 hours at room temperature (Scheme 1). Thus, unlike other coordinatively unsaturated acylrhodium complexes,[1b, 11, 15] **4** is surprisingly stable towards decarbonylation. Apparently, since the acyl ligand is located in the apical position (Figure 2), the *cis* coordination site required for decarbonylation is not available.[16] This result also indicates that the triflate ligand does not readily dissociate from the Rh^{III} complex in benzene. Surprisingly, unlike **1** and **2**, complex **3** does not react with MeCHO or PhCHO under the same conditions, or even after two days with a 100-fold excess of benzaldehyde.

The nucleophilicity of **1** was compared with that of the chloro complexes **2** and **3**, using MeI as an electrophile. The addition of MeI to rhodium(I) complexes is a classical, well-studied reaction of industrial significance, which usually proceeds smoothly and is routinely used as a method for the formation of Rh–C bonds.[17] As expected, complexes **2** and **3** react smoothly with a stoichiometric amount of MeI in benzene at room temperature to yield the square-pyramidal complex *trans*-$[(iPr_3P)_2Rh(Cl)(I)(Me)]$ (**8**) (Me in the apical position) and the octahedral complex *mer*-$[(Et_3P)_3Rh(Cl)(I)(Me)]$ (**10**).[12, 18] The analogous reactions of MeI with $[(Cy_3P)_2RhCl]$ (Cy = cyclohexyl) and $[(Me_3P)_3RhCl]$ complexes result in $[(Cy_3P)_2Rh(Cl)(I)(Me)]$[19a] and $[(Me_3P)_3Rh(Cl)(I)(Me)]$,[19b] respectively. Interestingly, whereas **3** reacts readily with one equivalent of MeI even at −20 °C, no significant reaction of **1** with MeI (or with MeOTf) is observed after several hours at room temperature, even when a fivefold excess of MeI is used.

This difference in chemoselectivity is strikingly apparent in competitive experiments in which complexes **1**–**3** were treated with a 10-fold excess of a 1:1 molar mixture of MeI and RCHO (R = Me or Ph) in a solution of C_6D_6. *trans*-$[(iPr_3P)_2Rh(N_2)Cl]$ (**11**)[20] was also examined in the competitive experiments, and the results are presented in Table 1.

Table 1. Competitive reactivity of Rh^{I} complexes in oxidative addition reactions.

Complex	Substrates[a]	Products	Molar ratio of RCHO/MeI adducts[c]
1	MeCHO + MeI	MeCHO adduct **4**	100:0
	PhCHO + MeI	PhCHO adduct **12**[b]	100:0
2	MeCHO + MeI	mixture of **6**, **8**, **9**	80:20
	PhCHO + MeI	mixture of **5**, **8**, **9**	65:35
11	MeCHO + MeI	mixture of **6**, **7**, **8**, **9**	35:65
	PhCHO + MeI	mixture of **5**, **7**, **8**, **9**	15:85
3	MeCHO + MeI	mainly **10**	0:100
	PhCHO + MeI	mainly **10**	0:100

[a] Reaction conditions: room temperature, benzene solution, molar ratio of RCHO/MeI/Rh^{I} complex = 10:10:1. [b] Complex **12**, $[(i\text{Pr}_3\text{P})_2\text{Rh}(\text{OTf})(\text{H})(\text{COPh})]$, was synthesized analogously to **4**.[12] [c] The ratio is based on ^{31}P and ^{1}H NMR data. Compounds **7** and **9** are included in the total ratio of the addition products of RCHO and MeI, respectively.

It is apparent that the four similar Rh complexes behave very differently in the oxidative addition of aldehydes and MeI. $[(i\text{Pr}_3\text{P})_2\text{RhOTf}]$ (**1**) reacts selectively with aldehydes, leaving MeI untouched, but $[(\text{Et}_3\text{P})_3\text{RhCl}]$ (**3**) reacts selectively with MeI, leaving the aldehydes unconverted. Although the reactions of $[(i\text{Pr}_3\text{P})_2\text{RhCl}]_2$ (**2**) and *trans*-$[(i\text{Pr}_3\text{P})_2\text{Rh}(\text{N}_2)\text{Cl}]$ (**11**) under the same conditions are not selective, they exhibit opposite relative reactivity towards aldehydes and MeI.

Further studies are required to determine the reasons for the differences in reactivity and selectivity of the phosphane-rhodium(I) complexes; however, a possible explanation is that the oxidative addition of aldehydes requires a three-coordinate, 14-electron Rh^{I} complex, whereas the oxidative addition of MeI proceeds via the four-coordinate, 16-electron complex. The oxidative addition of aldehydes to $[(\text{Me}_3\text{P})_3\text{RhCl}]$ was shown to involve the 14-electron complex,[8] as were other C–H oxidative addition reactions to L_3RhCl, which proceed via a three-centered transition state.[21] On the other hand, MeI reacts with L_3RhCl by means of an $\text{S}_\text{N}2$-type mechanism, in which the four-coordinate complex is the active species.[17f, 17i, 22]

The lack of reactivity of **3**, and the lower reactivity of **11** with aldehydes than of **1** and **2**, may be due to the ability of **1** and **2** to easily generate the three-coordinate species in solution,[23] whereas phosphane dissociation from **3** and **11** may be more difficult.[24, 25] On the other hand, **3** reacts with MeI even at low temperatures, since the generation of the three-coordinate species is probably not required. Apparently, electron density at the metal center plays a key role in the addition of MeI.[26] Compound **2** is more reactive than **1**, probably due to the chloride ligand being a better donor than the triflate. Interestingly, the dimer **2** reacts preferentially with aldehydes, whereas the monomer **11** reacts preferentially with MeI. This result is in agreement with the greater ease of formation of a three-coordinate complex with **2**.[23a, 27]

This study demonstrates unprecedented ligand-controlled selectivity of similar rhodium(I) complexes in classical oxidative addition reactions. The reactivity of complexes of the type $[\text{P}_n\text{RhX}]$ is strongly dependent on the number and nature of the alkylphosphane (P) and the halide or triflate (X), and can be selectively directed to the oxidative addition of an aldehyde or MeI. The observed selectivity may be potentially useful in reactions where substrates containing formyl groups (and perhaps other groups with reactive nonpolar bonds) and electrophilic centers in the same system are involved. An example of high substrate selectivity in such mixtures is described herein.

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[2] H. Werner, J. Wolf, A. Höhn, *J. Organomet. Chem.* **1985**, *287*, 395.

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[5] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-150421 (**1**) and CCDC-150420 (**4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[6] To the best of our knowledge, besides Rh complexes,[4] only two complexes with η^2-coordinated triflate to a single metal center have been characterized: a) titanium: J. G. Donkervoort, J. T. B. H. Jastrzebski, B. J. Deelman, H. Kooijman, N. Veldman, A. L. Spek, G. van Koten, *Organometallics* **1997**, *16*, 4174; b) silver: D. Gudat, M. Schrott, V. Bajorat, M. Nieger, S. Kotila, R. Fleischner, D. Stalke, *Chem. Ber.* **1996**, *129*, 337; c) the proposed η^2 coordination of triflate in the manganese complex (L. S. Stuhl, E. L. Muetterties, *Inorg. Chem.* **1978**, *17*, 2148) may be incorrect, see ref. [6d]; d) for a review on coordinated triflates, see: G. A. Lawrance, *Chem. Rev.* **1986**, *86*, 17.

[7] G. M. Intille, *Inorg. Chem.* **1972**, *11*, 695.

[8] D. Milstein, *Acc. Chem. Res.* **1984**, *17*, 221, and references therein.

[9] a) D. Milstein, *Organometallics* **1982**, *1*, 1549; b) D. Milstein, *J. Chem. Soc. Chem. Commun.* **1982**, 1357; c) D. Milstein, *J. Am. Chem. Soc.* **1986**, *108*, 1336.

[10] C. Bianchini, A. Meli, M. Peruzzini, F. Vizza, *Organometallics* **1991**, *10*, 820, and references therein.

[11] K. Wang, T. J. Embe, A. S. Goldman, *Organometallics* **1995**, *14*, 4929.

[12] Selected spectroscopic data of compounds **4**, **6**, **8**, **10**, and **12**. All NMR spectra were measured on a Bruker DPX250 spectrometer at 25 °C in C_6D_6. Frequencies used: ^{1}H 250 MHz, ^{31}P 100 MHz, ^{13}C 62.5 MHz. Standards: ^{1}H NMR: $\text{C}_6\text{D}_5\text{H}$ ($\delta = 7.15$, internal); ^{31}P NMR: H_3PO_4 (aq., 85 %, $\delta = 0$, external); ^{13}C: C_6D_6 ($\delta = 128$, internal). **4**: $^{31}\text{P}\{^{1}\text{H}\}$ NMR: $\delta = 47.2$ (d, $^{1}J(\text{Rh,P}) = 129$ Hz, 2P); ^{1}H NMR: $\delta = 2.80$ (s, 3H; COCH_3), 2.20 (m, 6H; $\text{PC}H(\text{CH}_3)_2$), 1.08 (dvt, $J = 7.2$ Hz, 18H; $\text{PCH}(\text{C}H_3)_2$), 1.00 (dvt, $J = 6.9$ Hz, 18H; $\text{PCH}(\text{C}H_3)_2$), -19.23 (dt, $^{2}J(\text{Rh,H}) = 37$ Hz, $^{3}J(\text{P,H}) = 10$ Hz, 1H; RhH); IR (film): $\tilde{\nu} = 1695\,\text{cm}^{-1}$ (C=O). The structure of **4** was confirmed by X-ray structure analysis (Figure 2). **6**: $^{31}\text{P}\{^{1}\text{H}\}$ NMR: $\delta = 48.1$ (d, $^{1}J(\text{Rh,P}) = 127$ Hz, 2P); ^{1}H NMR: $\delta = 2.99$ (s, 3H; COCH_3), 2.32 (m, 6H; $\text{PC}H(\text{CH}_3)_2$), 1.18 (overlapped dvt, 36H; $\text{PCH}(\text{C}H_3)_2$), -15.49 (dt, $^{2}J(\text{Rh,H}) = 27.6$ Hz, $^{3}J(\text{P,H}) = 9.8$ Hz, 1H; RhH); IR (film): $\tilde{\nu} = 1687\,\text{cm}^{-1}$ (C=O). **8**: $^{31}\text{P}\{^{1}\text{H}\}$ NMR: $\delta = 20.8$ (d, $^{1}J(\text{Rh,P}) = 99.3$ Hz, 2P); ^{1}H NMR: $\delta = 2.95$ (m, 6H; $\text{PC}H(\text{CH}_3)_2$), 1.23 (overlapped dvt, 39H; $\text{PCH}(\text{C}H_3)_2$ and RhCH_3); $^{13}\text{C}\{^{1}\text{H}\}$ NMR: $\delta = -3.77$ (dt, $^{1}J(\text{Rh,C}) = 24.5$ Hz, $^{2}J(\text{P,C}) = 5.6$ Hz; RhCH_3). The structure of **8** was confirmed by X-ray structure analysis. **10**: $^{31}\text{P}\{^{1}\text{H}\}$ NMR: $\delta = 19.3$ (dt, $^{1}J(\text{Rh,P}) = 133.5$ Hz, $^{2}J(\text{P,P}) = 26.8$ Hz, 1P), 1.3 (dd, $^{1}J(\text{Rh,P}) = 94.7$ Hz, $^{2}J(\text{P,P}) = 26.8$ Hz, 2P); ^{1}H NMR: $\delta = 2.20$ (m, 12H; $\text{PRhP}(\text{C}H_2\text{CH}_3)_3$), 1.62 (m, 6H; $\text{ClRhP}(\text{C}H_2\text{CH}_3)_3$), 1.17 (m, $^{2}J(\text{Rh,H}) = 1.7$ Hz, 3H; RhCH_3), 1.00 (dt, $^{3}J(\text{P,H}) = 13.8$ Hz, $^{3}J(\text{H,H}) = 6.8$ Hz, 18H; $\text{PRhP}(\text{CH}_2\text{C}H_3)_3$), 0.75

(dt, $^3J(\mathrm{P,H}) = 13.6$ Hz, $^3J(\mathrm{H,H}) = 7.5$ Hz, 9H; $\mathrm{ClRhP(CH_2C}H_3)_3$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR: $\delta = 0.11$ (ddt, $^1J(\mathrm{Rh,C}) = 21.2$ Hz, ^2J(P (unique),C) = 8.2 Hz, ^2J(P(mutually *trans*),C) = 5.5 Hz, $\mathrm{RhCH_3}$). **12**: $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR: $\delta = 45.8$ (d, $^1J(\mathrm{Rh,P}) = 123$ Hz, 2P); ^{1}H NMR: $\delta = 8.09$ (m, 2H; COPh), 7.05 (m, 3H; COPh), 2.23 (m, 6H; $\mathrm{PC}H\mathrm{(CH_3)_2}$), 1.06 (dvt, $J = 6.9$ Hz, 18H; $\mathrm{PCH(C}H_3)_2$), 0.99 (dvt, $J = 7.0$ Hz, 18H; $\mathrm{PCH(C}H_3)_2$), -20.92 (dt, $^2J(\mathrm{Rh,H}) = 44.5$ Hz, $^3J(\mathrm{P,H}) = 10$ Hz, 1H; RhH); IR (film): $\tilde{\nu} = 1650\,\mathrm{cm^{-1}}$ (C=O).

[13] I. El-Idrissi, O. Eisenstein, Y. Jean, *New. J. Chem.* **1990**, *14*, 671.

[14] Complex **6** was prepared from **2** and a small excess of MeCHO in benzene at room temperature.

[15] a) Coordinatively saturated acylrhodium–hydride complexes undergo decarbonylation via unsaturated intermediates.[8, 9a] b) The coordinatively unsaturated $[\mathrm{(Et_3P)_2Rh(Cl)(MeCO)(H)}]$ complex cannot be observed at room temperature. It undergoes immediate decarbonylation, evolving methane.

[16] However, **4** rapidly decomposes upon heating at 55 °C for 1 hour. A similar reactivity was observed in the case of six-coordinate acylrhodium–hydride complexes.[9a]

[17] Selected references: a) R. F. Heck, *J. Am. Chem. Soc.* **1964**, *86*, 2796; b) D. N. Lawson, J. A. Osborn, G. Wilkinson, *J. Chem. Soc. A* **1966**, 1733; c) S. Franks, F. R. Hartley, J. R. Chipperfield, *Inorg. Chem.* **1981**, *20*, 3238; d) D. Forster, *Adv. Organomet. Chem.* **1979**, *17*, 255; e) A. Haynes, B. E. Mann, G. E. Morris, P. M. Maitlis, *J. Am. Chem. Soc.* **1993**, *115*, 4093; f) P. M. Maitlis, A. Haynes, G. J. Sunley, M. J. Howard, *J. Chem. Soc. Dalton Trans.* **1996**, 2187, and references therein; g) T. R. Griffin, D. B. Cook, A. Haynes, J. M. Pearson, D. Monti, G. E. Morris, *J. Am. Chem. Soc.* **1996**, *118*, 3029; h) J. Rankin, A. C. Benyei, A. D. Poole, D. J. Cole-Hamilton, *J. Chem. Soc. Dalton Trans.* **1999**, 3771; i) L. Gonsalvi, H. Adams, G. L. Sunley, E. Ditzel, A. Haynes, *J. Am. Chem. Soc.* **1999**, *121*, 11233; j) for a recent review on MeI addition to $\mathrm{Rh^I}$ complexes, see: P. R. Sharp in *Comprehensive Organometallic Chemistry II, Vol. 8* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson, J. D. Atwood), Pergamon, **1995**, pp. 190–200, and references therein.

[18] The formation of **8** and **10** in the reaction of MeI with **2** and **3**, respectively, is accompanied by side products (20–40 % depending on the temperature and on the amount of MeI added). Presumably, diiodide complexes are formed as was reported.[19a] In the case of the reaction of **2** or **11** with MeI (see also Table 1), we observed the formation of *trans*-$[(i\mathrm{Pr_3P})_2\mathrm{Rh(I)_2Me}]$ (**9**) as a by-product.

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[21] a) J. A. Maguire, A. Petrillo, A. S. Goldman, *J. Am. Chem. Soc.* **1992**, *114*, 9492, and references therein; b) C. T. Spillett, P. C. Ford, *J. Am. Chem. Soc.* **1989**, *111*, 1932; c) P. C. Ford, T. L. Netzel, C. T. Spillett, D. B. Pourreau, *Pure Appl. Chem.* **1990**, *62*, 1091.

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[23] a) Complex **2** was found to be monomeric in benzene: D. Schneider, H. Werner, *Angew. Chem.* **1991**, *103*, 710; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 700. b) We have observed that complex **1** reacts with $[\{\mathrm{(cyclooctene)_2RhCl}\}_2]$ in benzene to give monophosphane complexes, indicating the dissociation of $i\mathrm{Pr_3P}$.

[24] In contrast to compound **3**, $[\mathrm{(Me_3P)_3RhCl}]$ is reported to react with an excess of MeCHO and PhCHO to give acyl hydride complexes.[8, 9a] The reason for the higher reactivity of $[\mathrm{(Me_3P)_3RhCl}]$ over $[\mathrm{(Et_3P)_3RhCl}]$ with aldehydes is not clear. It may be due to an associative phosphane displacement, preceded by coordination of the aldehyde, which is easier with a lower bulk at the metal center.

[25] Since complexes **2** and **11** show different selectivities in the reaction with a mixture of MeI and aldehyde, different intermediates are likely to be involved; hence we propose the dissociation of phosphane rather than that of $\mathrm{N_2}$ from **11**. Nitrogen does not readily dissociate from **11**: D. L. Thorn, T. H. Tulip, J. A. Ibers, *J. Chem. Soc. Dalton Trans.* **1979**, 2022.

[26] Electron-donating ligands coordinated to $\mathrm{Rh^I}$ centers facilitate the oxidative addition of MeI, see for example: a) S. S. Basson, J. G. Leipoldt, A. Roodt, J. A. Venter, T. J. Van Der Walt, *Inorg. Chem. Acta* **1986**, *119*, 35; b) G. J. Van Zyl, G. J. Lampbrecht, J. G. Leipoldt, T. W. Swaddle, *Inorg. Chem. Acta* **1986**, *143*, 223; c) see also ref. [17c] and [17i], and references therein.

[27] A similar tendency is observed with the dimer $[\{\mathrm{(Et_3P)_2Rh(Cl)}\}_2]$, which unlike the monomer **3**, reacts slowly with aldehydes at room temperature, giving predominantly carbonyl complexes.[15b]

Quasi One-Dimensional Organic Superconductor MDT-TSF · $\mathrm{AuI_2}$ with $T_c = 4.5$ K at Ambient Pressure[**]

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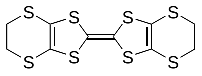
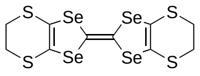
Tetsuo Otsubo,* Hiroshi Fukuoka, and Shoji Yamanaka

Although the first organic superconductors were prepared from radical-cation salts (Bechgaard salts) based on tetramethyltetraselenafulvalene (TMTSF) under extremely cryogenic conditions ($T_c < 1.4$ K), higher T_c superconductors were developed from heterocycle-fused tetrathiafulvalenes (TTFs), represented by bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF).[1] Whereas the Bechgaard salts have quasi one-dimen-


BEDT-TTF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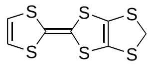
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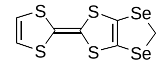
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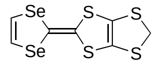
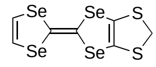

MDT-STF


MDT-TSF **1**

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