

## Efficient water-soluble catalytic system Rh<sup>I</sup>-CAP for biphasic hydroformylation of olefins

Oleg L. Eliseev,<sup>\*a</sup> Tatyana N. Bondarenko,<sup>a</sup> Sergey N. Britvin,<sup>b</sup>  
 Polina P. Khodorchenko<sup>a,c</sup> and Albert L. Lapidus<sup>a,c</sup>

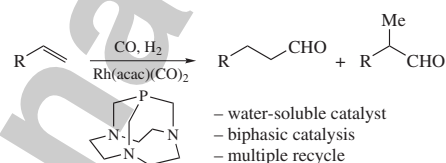
<sup>a</sup> N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. E-mail: oleg@server.ioc.ac.ru

<sup>b</sup> Department of Crystallography, St. Petersburg State University, 199034 St. Petersburg, Russian Federation

<sup>c</sup> I. M. Gubkin Russian State University of Oil and Gas, 119991 Moscow, Russian Federation

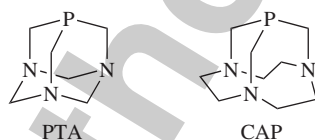
DOI: 10.1016/j.mencom.2018.05.011

**Rhodium-catalysed hydroformylation of styrene and aliphatic olefins under biphasic conditions in the presence of water-soluble 1,4,7-triaza-9-phosphatricyclo[5.3.2.1<sup>4,9</sup>]tridecane (CAP) chemoselectively affords aldehydes. Multiple catalyst reuse without loss in performance is demonstrated.**



Hydroformylation of alkenes is one of the most important transition metal catalysed reactions with huge industrial implementation.<sup>1–3</sup> Modified rhodium catalysts are widely used because of high reaction rate at low pressure and temperature.<sup>4</sup> Molecular and electronic structure of supporting ligand plays a crucial role in catalyst composition, governing its activity, chemo- and regioselectivity. Although a large number of ligands have been proposed to this reaction,<sup>5–7</sup> development of new ones remains topical. Among them, water-soluble species attract special attention because they can immobilize rhodium in aqueous phase thus solving problem of catalyst separation and reuse.<sup>7</sup> In particular, tris(3-sulfophenyl)phosphine sodium salt (TPPTS)<sup>8</sup> found commercial application in Ruhrchemie/Rhône-Poulenc biphasic process of propene hydroformylation into butanal.<sup>9,10</sup> Besides TPPTS and other sulfonated phosphanes,<sup>11–16</sup> other types of water-soluble ligands in olefin hydroformylation are scarce.<sup>17–19</sup>

Recently cationic water-soluble phosphanes, *e.g.*, tricyclic cage 1,3,5-triaza-7-phosphaadamantane (PTA) and its derivatives, attract increasing interest in catalysis and medicinal chemistry.<sup>20,21</sup> The distinctive features of PTA are sterically undemanding adamantane structure, water solubility, chemical and thermal stability. The Rh-PTA complexes were tested, among some other transition metal catalysed reactions, in olefin hydroformylation.<sup>22–24</sup>



Very recently we accessed a new symmetric cage-like triaza-phosphane, *viz.* 1,4,7-triaza-9-phosphatricyclo[5.3.2.1.4,9]tridecane (CAP) possessing a tris(homoadamantane) cage architecture (*cf.* refs. 25, 26). Like PTA, CAP is solid, air- and thermally stable water-soluble phosphane. From the structural point of view, both phosphanes can be regarded as macrocyclic homologues. However, computations of Tolman's electronic parameter show that CAP possesses essentially higher electron-donating ability than PTA and in this respect approaches strong donors such as tri-*tert*-

butylphosphane and tricyclohexylphosphane.<sup>25</sup> Large differences between the <sup>31</sup>P NMR chemical shifts of CAP (+47 ppm) and PTA (–96 ppm) were detected along with unusual atrane-like steric behavior.<sup>26</sup> Unusual stereoelectronic properties of CAP in combination with its hydrophilicity make it an interesting candidate for study of its catalytic activity. Indeed, Rh(acac)(CO)<sub>2</sub>/CAP turned out to be very active and selective system in hydroformylation of styrene and aliphatic olefins.

We chose Rh(acac)(CO)<sub>2</sub> as a popular rhodium source and at first compared its performance in combination with CAP, PTA and triphenylphosphine ligands under one- and two-phase conditions. IR spectra of Rh(acac)(CO)<sub>2</sub> and Rh(acac)(CO)<sub>2</sub> + 2 CAP were recorded in dichloromethane. Symmetric and asymmetric CO stretches of Rh(acac)(CO)<sub>2</sub> are at 2084 and 2012 cm<sup>–1</sup>, which corresponds to reported data.<sup>29</sup> Addition of two equivalents of CAP to Rh(acac)(CO)<sub>2</sub> solution leads to disappearing these bands and arising a new one at 1962 cm<sup>–1</sup>. We conclude that one carbonyl ligand in Rh coordination sphere is replaced by CAP giving Rh(acac)(CO)(CAP) complex. Reported ν(CO) frequencies for analogous complexes Rh(acac)(CO)(PPh<sub>3</sub>), Rh(acac)(CO)(PPhC<sub>6</sub>H<sub>4</sub>)<sub>2</sub> and Rh(acac)(CO)(PCy<sub>3</sub>) are 1977, 1968 and 1959 cm<sup>–1</sup>, respectively.<sup>30</sup> One can conclude that electron-donor ability of CAP ligand is high and comparable with that of PCy<sub>3</sub>, as has been predicted by DFT computations in our previous work.<sup>25</sup>

Catalyst activity was estimated based on olefin conversion and average turnover frequency (TOF) which was calculated as amount of formed aldehydes per mole of Rh per hour (Table 1). In hydroformylation of styrene in toluene solution, PPh<sub>3</sub> gave more active catalyst than CAP. Nevertheless, selectivity to branched aldehyde is much higher for the latter (entries 1, 2). In biphasic toluene + water medium, both activity and regioselectivity of Rh(acac)(CO)<sub>2</sub> + 2 CAP system increased substantially as TOF reached 285 h<sup>–1</sup> and branched to linear aldehyde ratio was of 94 : 6, more than three times higher than that under single phase conditions (entry 3). Under the same reaction conditions, the combination of Rh(acac)(CO)<sub>2</sub> and PTA seemed to be much less active and unselective, both isomeric aldehydes were formed in almost the same amount (entry 4). As Tolman cone angles of both ligands are close, observed dramatic difference in activity

**Table 1** Hydroformylation of olefins in the presence of Rh(acac)(CO)<sub>2</sub> and various ligands.<sup>a</sup>

$$\text{R-CH=CH}_2 + \text{CO} + \text{H}_2 \xrightarrow[\text{ligand}]{\text{Rh(acac)(CO)}_2} \text{R-CH}_2\text{-CH}_2\text{-CHO} + \text{R-CH(Me)-CHO}$$

Entry	Substrate	Solvent	Ligand, L:Rh molar ratio	T/°C	P/bar	Conversion (%)	Average TOF/h <sup>-1</sup>	Branched/linear ratio
1	Styrene	Toluene	PPh <sub>3</sub> , 2	80	20	100	479	62:38
2	Styrene	Toluene	CAP, 2	80	20	28	133	82:18
3	Styrene	Toluene–H <sub>2</sub> O	CAP, 2	80	20	60	285	94:6
4	Styrene	Toluene–H <sub>2</sub> O	PTA, 2	80	20	17	75	55:45
5	Styrene	Toluene–H <sub>2</sub> O	CAP, 3	80	20	78	381	94:6
6	Styrene	Toluene–H <sub>2</sub> O	CAP, 4	80	20	79	390	93:7
7	Styrene	Toluene–H <sub>2</sub> O	CAP, 2	80	10	24	105	87:13
8	Styrene	Toluene–H <sub>2</sub> O	CAP, 2	80	30	73	358	94:6
9	Styrene	Toluene–H <sub>2</sub> O	CAP, 3	60	20	37	178	98:2
10	Styrene	Toluene–H <sub>2</sub> O	CAP, 3	100	20	67	319	81:19
11	Hex-1-ene	H <sub>2</sub> O	CAP, 1	80	20	37	183	28:72
12	Hex-1-ene	H <sub>2</sub> O	CAP, 2	80	20	55	258	29:71
13	Hex-1-ene	H <sub>2</sub> O	CAP, 3	80	20	40	194	30:70
14	Hex-1-ene	H <sub>2</sub> O	PTA, 2	80	20	13	55	26:74
15	Hex-1-ene	H <sub>2</sub> O	CAP, 2	80	30	58	266	30:70
16	Non-1-ene	H <sub>2</sub> O	CAP, 2	80	20	35 <sup>b</sup>	174	28:72
17	Dodec-1-ene	H <sub>2</sub> O	CAP, 2	80	20	50 <sup>b</sup>	230	27:73

<sup>a</sup>Run conditions: olefin (4.4 mmol), Rh(acac)(CO)<sub>2</sub> (0.0044 mmol), ligand, toluene (optionally, 5 ml), H<sub>2</sub>O (optionally, 2 ml), 2 h. <sup>b</sup>In addition to aldehydes, internal olefins are also formed (8 and 14% for entries 16, 17, respectively).

and regioselectivity should be attributed to their different basicity rather than steric hindrance.<sup>25</sup>

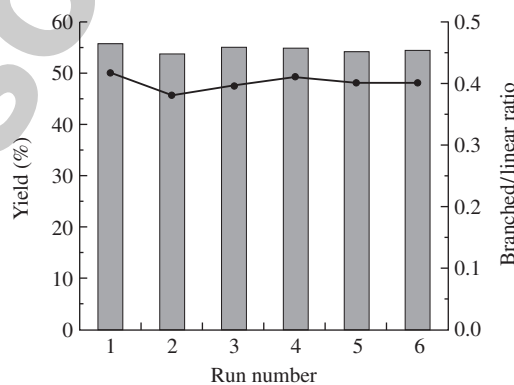
Raising CAP:Rh ratio from 2:1 to 3:1 led to substantial increase in activity while regioselectivity remained the same. Further increase in CAP amount gave almost no activity gain and disproved the selectivity (entries 3, 5, 6). We conclude that CAP:Rh ratio of 3:1 is optimal. Syngas pressure promotes both catalyst activity and selectivity to 2-phenylpropanal (entries 7, 8). Reaction temperature of 80 °C seems to be optimal. Raising temperature to 100 °C resulted in decreasing both activity and regioselectivity (entries 5, 10). At 60 °C, branched to linear aldehyde ratio was very high, however, styrene conversion was poor (entry 9).

Next, we examined CAP in hydroformylation of neat hex-1-ene. As expected, linear heptanal was the favoured product, with branched to linear aldehyde ratio being 29:71. Remarkably, regioselectivity was almost unaffected by changing CAP:Rh ratio (entries 11–13). By increasing syngas pressure to 30 bar, an insignificant improvement in selectivity to branched aldehyde was achieved (entry 15). For comparison, we tested PTA under the same reaction conditions and found that hexene conversion was much lower (entries 12, 14).

In hydroformylation of hex-1-ene with CAP ligand, no migration of double bond in the substrate occurs. We detected only trace amount of internal hexenes in reaction mixture of some runs (<0.2%). On the contrary, PTA gives considerable amount of isomers under the same conditions (entry 14). However, for higher homologues such as non-1-ene and dodec-1-ene double bond migration occurs with CAP, too. The thus formed less reactive internal olefins (8 and 14% yields, entries 16, 17, respectively) do not undergo hydroformylation.

Note that excellent chemoselectivity of Rh(acac)(CO)<sub>2</sub> + CAP system was determined. In all experiments with this ligand, hydrogenation products (ethylbenzene, alkanes) were absent in the reaction mixture or detected in trace amounts. Reportedly, electron-donating phosphanes promote direct formation of alcohols under hydroformylation conditions in protic solvents.<sup>27,28</sup> However, no alcohols were formed in our experiments with CAP.

We performed catalyst recycling in hydroformylation of hex-1-ene. Run conditions were the same as for entry 12. In six



**Figure 1** Yields of products (columns) and branched/linear ratio (line) in catalyst recycling in hex-1-ene hydroformylation (for the reaction conditions, see Table 1, entry 12).

sequent runs, substrate conversion, aldehydes yield and branched to linear aldehyde ratio were almost unchanged (Figure 1).

In conclusion, water-soluble cage-like triazaphosphine CAP was successfully applied for the first time as a stabilising ligand for Rh<sup>I</sup>-catalysed biphasic hydroformylation of styrene and aliphatic olefins. In styrene hydroformylation, excellent activity and regioselectivity to branched aldehyde were achieved. Attractive feature of the catalyst is high chemoselectivity, aldehydes always are the sole products. Catalyst can be easily separated from the products by simple decantation of the organic layer of the reaction mixture. Multiple catalyst reuse without loss in performance was demonstrated. Thus, proposed catalytic system promises a shortcut access to 2-arylpropionic aldehydes, valuable precursors of pharmaceutical products of the Profen class.<sup>31,32</sup>

This work was supported by the St. Petersburg State University (grant nos. 0.37.235.2015 and 3.37.222.2015).

## References

- M. Beller, B. Cornils, C. D. Frohning and C. W. Kohlpaintner, *J. Mol. Catal. A: Chem.*, 1995, **104**, 17.
- G. D. Frey, *J. Organomet. Chem.*, 2014, **754**, 5.

- 3 H.-W. Bohner and B. Cornils, *Adv. Catal.*, 2002, **47**, 1.
- 4 *Rhodium Catalyzed Hydroformylation*, eds. P. W. N. M. van Leeuwen and C. Claver, Kluwer Academic Publishers, Dordrecht, 2002.
- 5 J. Klosin and C. R. Landis, *Acc. Chem. Res.*, 2007, **40**, 1251.
- 6 R. Franke, D. Selent and A. Börner, *Chem. Rev.*, 2012, **112**, 5675.
- 7 A. M. Trzeciak and J. J. Ziólkowski, *Coord. Chem. Rev.*, 1999, **190–192**, 883.
- 8 E. G. Kuntz, *Chemtech*, 1987, **17**, 570.
- 9 B. Cornils and E. G. Kuntz, in *Aqueous-Phase Organometallic Catalysis*, eds. B. Cornils and W. A. Herrmann, Wiley–VCH, Weinheim, 1998, pp. 271–339.
- 10 C. W. Kohlpaintner, R. W. Fischer and B. Cornils, *Appl. Catal. A*, 2001, **221**, 219.
- 11 I. Willner and R. Maidan, *J. Chem. Soc., Chem. Commun.*, 1988, 876.
- 12 H. Bahrmann, K. Bergrath, H.-J. Kleiner, P. Lappe, C. Naumann, D. Peters and D. Regnat, *J. Organomet. Chem.*, 1996, **520**, 97.
- 13 S. Bischoff and M. Kant, *Ind. Eng. Chem. Res.*, 2000, **39**, 4908.
- 14 S. Bischoff and M. Kant, *Catal. Today*, 2001, **66**, 183.
- 15 T. Suárez, B. Fontal, G. León, M. Reyes, F. Bellandi, R. R. Contreras and P. Cancines, *Trans. Metal Chem.*, 2006, **31**, 974.
- 16 T. Hamerla, A. Rost, Y. Kasaka and R. Schomäcker, *ChemCatChem*, 2013, **5**, 1854.
- 17 E. Mieczysława, A. M. Trzeciak and J. J. Ziólkowski, *J. Mol. Catal. A: Chem.*, 1999, **148**, 59.
- 18 S. U. Son, J. W. Han and Y. K. Chung, *J. Mol. Catal. A: Chem.*, 1998, **135**, 35.
- 19 T. Borrmann, H. W. Roesky and U. Ritter, *J. Mol. Catal. A: Chem.*, 2000, **153**, 31.
- 20 A. D. Phillips, L. Gonsalvi, A. Romerosa, F. Vizza and M. Peruzzini, *Coord. Chem. Rev.*, 2004, **248**, 955.
- 21 J. Bravo, S. Bolaño, L. Gonsalvi and M. Peruzzini, *Coord. Chem. Rev.*, 2010, **254**, 555.
- 22 F. P. Pruchnik, P. Smoleński, E. Galdecka and Z. Galdecki, *New J. Chem.*, 1998, **22**, 1395.
- 23 F. P. Pruchnik, P. Smoleński and K. Wajda-Hermanowicz, *J. Organomet. Chem.*, 1998, **570**, 63.
- 24 A. D. Phillips, S. Bolaño, S. S. Bosquain, J.-C. Daran, R. Malacea, M. Peruzzini, R. Poli and L. Gonsalvi, *Organometallics*, 2006, **25**, 2189.
- 25 S. N. Britvin and A. Lotnyk, *J. Am. Chem. Soc.*, 2015, **137**, 5526.
- 26 S. N. Britvin, A. M. Romyantsev, A. E. Zobnina and M. V. Padkina, *Chem. Eur. J.*, 2016, **22**, 14227.
- 27 J. K. MacDougall and D. J. Cole-Hamilton, *J. Chem. Soc., Chem. Commun.*, 1990, 165.
- 28 J. K. MacDougall, M. C. Simpson, M. J. Green and D. J. Cole-Hamilton, *J. Chem. Soc., Dalton Trans.*, 1996, 1161.
- 29 T. P. Dougherty, W. T. Grubbs and E. J. Heilweil, *J. Phys. Chem.*, 1994, **98**, 9396.
- 30 A. Brink, A. Roodt, G. Steyl and H. G. Visser, *Dalton Trans.*, 2010, **39**, 5572.
- 31 F. A. Rampf and W. A. Herrmann, *J. Organomet. Chem.*, 2000, **601**, 138.
- 32 D. Giacomini, P. Galletti, A. Quintavalla, G. Gucciardo and F. Paradisi, *Chem. Commun.*, 2007, 4038.

Received: 14th November 2017; Com. 17/5407