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Macrocyclic Pd(II) dithiolate complexes as catalysts in Heck reactions

Pravin A. Mane, Sandip Dey, K.V. Vivekananda

Macrocyclic Pd(II) dithiolate complexes as catalysts in Heck reactions

Pravin A. Mane, Sandip Dey[*] and K. V. Vivekananda

Chemistry Division, Bhabha Atomic Research Center, Mumbai 400 085, India

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ABSTRACT

The supramolecular palladium dithiolate complexes, $[Pd_2(dppe)_2\{S(C_6H_4)_nS\}]_2(OTf)_4$ and $[Pd_2(dppe)_2(SCH_2C_6H_4CH_2S)]_4(OTf)_8$ (dppe = 1,2-bis(diphenylphosphino)ethane) has been investigated as highly stable and robust catalysts in Heck C-C coupling reactions. The arylation of butyl acrylate and styrene with various aryl bromides under optimized catalytic systems, showed excellent yield and turnover number (410000) of the products. The tertranuclear complexes showed slightly higher catalytic activity than the octanuclear complex.

The palladium catalyzed Heck coupling reaction has evolved as an important carbon–carbon bond forming reaction in organic synthesis,[1] and the development of new catalysts is a continuing process. The nature of ligand bonded to the Pd center plays the most vital role in improving the reaction condition and catalytic activity among all other parameters such as base, media, temperature, additive, etc.[2] In the early literature of catalysts, palladium complexes of bulky or electron rich phosphine[3,4] and later nitrogen-containing or N-heterocyclic carbene ligands[5,6] are reported as active catalyst precursors in various C–C coupling reactions. Such ligands are often expensive, air- and moisture-sensitive, the difficulty in preparation and handling limits their industrial applications.[2,7] There has been consistent effort to develop inexpensive, stable and highly effective phosphine free catalysts which can work under mild experimental conditions as well as in low catalyst loading. The use of high turnover number (TON) catalysts can also reduce cost and contamination in the preparation of pharmaceuticals, additionally their recycling may be avoided.[7]

Alternatively the ligands containing group 16 donor atoms, sulfur[8-18] and selenium,[10,14,15,21-25] owing to strong electron-donating property and bonding to the metal center, their palladium complexes have been recently emerged as highly efficient and stable catalysts. The sulfur ligands remained unexplored for long time in the catalyst design, due to the misbelief as catalyst poison[26], however they are now considered as catalyst promoter.[27] A plethora of Pd complexes with thiolate,[8] thiourea,[9] hybrid thiolate (NS,[10,11] PS[12]), thioether[13,14] and Schiff base[15] type ligands, have been developed as phosphine free, efficient catalysts in Heck and Suzuki C–C coupling reactions. The carbene (CS[16]), *ortho*-metalated (CS,[17] CNS[18]) and pincer type (SCS,[17,19] SNS[20]) palladacycles containing sulfur moieties also have shown excellent activity. In addition, the Pd nanoparticles, capped by thiols which can simultaneously act as reductants and protecting groups, have also been employed as catalysts in C–C coupling[28,29] and Heck reactions.[30] Each of these catalyst systems has distinct properties and advantages.

We also recently evaluated the catalytic activity of chalcogenolate,[10,24] chalcogenoether[25] and supramolecular[31] Pd complexes in Suzuki and Sonogashira reactions. So far, only a few supramolecular dendritic[32] and self-assembled palladium complexes[33] with amphiphilic phosphine ligands have been reported as catalysts in C–C coupling reactions. The example of supramolecular co-ordination complex of palladium thiolates is almost rare, due to high tendency of the ligands forming bridge between two metal centers, thus often result insoluble polymeric compounds. The supramolecular complexes $[Pd_2(dppe)_2\{S(C_6H_4)_nS\}]_2(OTf)_4$ and $[Pd_2(dppe)_2(SCH_2C_6H_4CH_2S)]_4(OTf)_8$ (Chart 1) developed by us, are discrete macrocyclic molecules, in which the S atoms of the dithiolate ligands form three connecting bonds.[31] These Pd dithiolate complexes showed excellent catalytic activity in Suzuki cross coupling reactions with high TON.[31] Motivated by these preliminary results, we decided to investigate their catalytic activities in Heck coupling reactions (Scheme 1).

R = CH_3, $COCH_3$; R_1 = Ph, $COOBu^n$
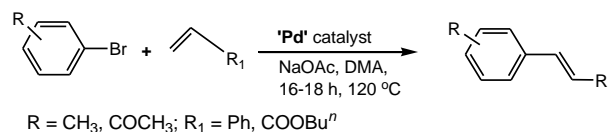
Scheme 1. Heck coupling reaction of aryl bromide with butyl acrylate and styrene

In this letter the arylation of butyl acrylate and styrene with an aryl bromide are used as model reactions. The optimization

∗ Corresponding author. Tel.: +91-22-25592589; e-mail: dsandip@barc.gov.in

studies, the comparative activity of different macrocycles, low loading and reusability of the catalyst etc. will be discussed herein.
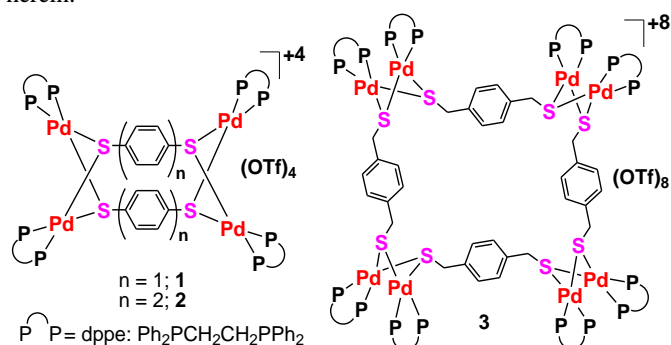

Chart 1. Palladium dithiolate complexes used as catalysts in Heck reaction

The reaction conditions were optimized with respect to solvent, base, temperature and time in the coupling of both *n*-butyl acrylate and styrene with aryl bromide using **1** as catalyst (Table 1-2). Initially the yield of the model reaction, the coupling of non-activated tolyl bromide and styrene was low which was improved by the addition of tetra-*n*-butyl ammonium bromide (TBAB). In case of coupling reactions of activated aryl bromide 4-bromoacetophenone and styrene, TBAB was not used for the optimization of time and temperature. As the yields of the reactions of 4-bromoacetophenone and *n*-butyl acrylate were comparatively low, TBAB was invariably added in all the four set of reactions (Table 1). Although the polar aprotic solvents are generally established as preferred medium for Heck reactions, the

Table 1

Optimization of reaction parameters[a]

Entry	Solvent	Base	Temp (°C)	Time (h)	Yield (%)
Effect of Solvent					
1	DMA	NaOAC	120	16	100
2	DMF	NaOAC	120	16	97
3	Toluene	NaOAC	120	16	60
Effect of Base					
4	DMA	NaOAC	120	16	100
5	DMA	Na_2CO_3	120	16	89
6	DMA	Et_3N	120	16	50
7	DMA	Bu_4NOH	120	16	-
Effect of Temperature					
8	DMA	NaOAC	120	16	100
9	DMA	NaOAC	100	16	47
10	DMA	NaOAC	80	16	31
Effect of Time					
11	DMA	NaOAC	120	24	100
12	DMA	NaOAC	120	18	99
13	DMA	NaOAC	120	12	76

[a] Reaction conditions: 4-Bromoacetophenone (1.0 mmol), butyl acrylate (1.5 mmol), base (1.5 mmol) in H_2O, DMA (3 mL), TBAB (1 mmol) added, 0.4 mol% of Pd (**1**).

Table 2
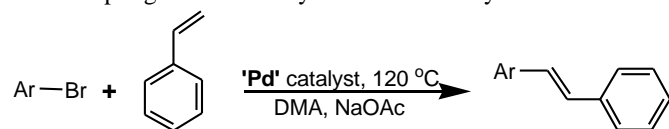
Optimization of reaction parameters[a]

Entry	R	Solvent	Base	Temp (°C)	Time (h)	Yield (%)
Effect of Solvent[b]						
1	4-CH_3	DMA	NaOAC	120	16	75
2	4-CH_3	DMF	NaOAC	120	16	43
3	4-CH_3	Toluene	NaOAC	120	16	28
Effect of Base[b]						
4	4-CH_3	DMA	NaOAC	120	16	75
5	4-CH_3	DMA	Na_2CO_3	120	16	64
6	4-CH_3	DMA	K_2CO_3	120	16	40
Effect of Temperature						
7	4-$COCH_3$	DMA	NaOAC	120	16	100
8	4-$COCH_3$	DMA	NaOAC	110	16	69
9	4-$COCH_3$	DMA	NaOAC	100	16	58
10	4-$COCH_3$	DMA	NaOAC	80	16	27
Effect of Time						
11	4-$COCH_3$	DMA	NaOAC	120	16	100
12	4-$COCH_3$	DMA	NaOAC	120	12	79
13	4-$COCH_3$	DMA	NaOAC	120	8	66
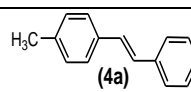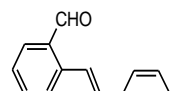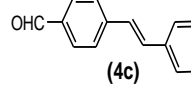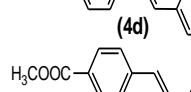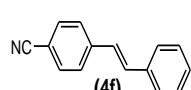
[a] Reaction conditions: Aryl bromide (1.0 mmol), styrene (1.5 mmol), base (2 mmol) in H_2O, DMA (3 mL), 0.4 mol% of Pd (**1**). [b] TBAB (1 mmol) added.

solvents DMF, DMA and toluene were screened. In both the coupling reactions of *n*-butyl acrylate and styrene, DMA was found to be the preferred solvent. The polar solvent DMF gave quantitative yield in case of reaction with *n*-butyl acrylate, however the non polar solvent toluene was not very effective in both the cases. The solvent toluene has be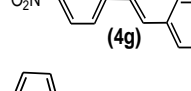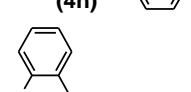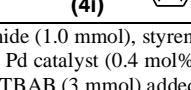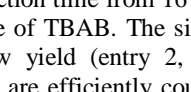en reported to improve the rate of Heck reaction[34] giving moderate yield which is comparatively lower than in DMA or DMF. Among the bases NaOAc was found to be a superior over Na_2CO_3, whereas the organic bases Et_3N and Bu_4NOH gave lower yield or no products (Table 1, entries 6-7). This trend was observed in optimization studies of most of the Heck reactions,[35] albeit Et_3N has been reported to yield higher than inorganic bases in few reactions.[36] The investigations at different temperatures within 80-120 °C were carried out in the coupling reactions of both styrene and n-butyl acrylate with 4-bromoacetophenone, for the latter TBAB was used. In both the cases 100% yield was obtained at reaction temperature 120 °C. As expected the catalytic activity is diminished at lower temperatures. Using the above optimized conditions such as DMA as solvent, NaOAc as base and temperature at 120 °C, the reaction times were varied to get the quantitative yield of product within 16 and 18 hrs for the coupling of styrene and n-butyl acrylate, respectively.

Having established the optimum reaction conditions in terms of solvent, base and temperature, the catalytic activity of the complexes was evaluated in Heck reaction of alkenes and a wide range of aryl bromides (Table 3-4). It is noteworthy that the catalytic system is tolerant to wide range of functional groups such as CHO, COMe, COOMe, CN and NO_2. The coupling reaction of unactivated 4-bromotoluene and styrene resulted low yield (28%) in the presence of 1 mmol of TBAB (entry 1, Table 3), which could be improved to moderate or good yield (59-75%) on addition of 3 mmol of TBAB for the three catalyst systems.

Table 3
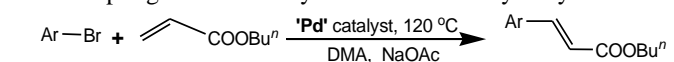Heck coupling reaction of aryl bromide with styrene[a]

$Ar-Br$ + styrene → $\overset{\text{'Pd' catalyst, 120 °C}}{\underset{\text{DMA, NaOAc}}{\longrightarrow}}$ Ar—CH=CH—Ph

Entry	ArBr	Product	Yield (%)
1	4-CH$_3$C$_6$H$_4$Br	(4a)	1: 28[b] 1: 75[c] 2: 64[c] 3: 59[c] 3: 25[d]
2	2-OHCC$_6$H$_4$Br	(4b)	1: 99
3	4-OHCC$_6$H$_4$Br	(4c)	2: 98
4	4-CH$_3$COC$_6$H$_4$Br	(4d)	1: 100 2: 95 3: 89
5	4-CH$_3$COOC$_6$H$_4$Br	(4e)	1: 83 1: 90[b] 1: 97[c] 2: 90[c]
6	4-NCC$_6$H$_4$Br	(4f)	1: 87 1: 93[c] 3: 83[c]
7	4-O$_2$NC$_6$H$_4$Br	(4g)	1: 89 1: 93[c]
8	2-C$_4$H$_3$SBr	(4h)	2: 43[c]
9	4-C$_9$H$_6$NBr	(4i)	1: 80[c]
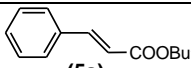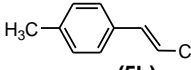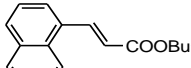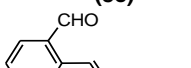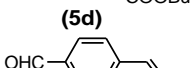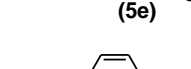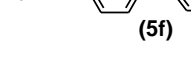
[a] Reaction conditions: Aryl bromide (1.0 mmol), styrene (1.5 mmol), NaOAc (2 mmol) in H$_2$O, DMA (3 mL), Pd catalyst (0.4 mol% of Pd), 120 °C, time: 16 h. [b] TBAB (1 mmol) added. [c] TBAB (3 mmol) added. [d] time: 24 h.

Table 4
Heck coupling reaction of aryl bromide with butyl acrylate[a]

$Ar-Br$ + =COOBu^n $\overset{\text{'Pd' catalyst, 120 °C}}{\underset{\text{DMA, NaOAc}}{\longrightarrow}}$ Ar—CH=CH—COOBu^n

Entry	ArBr	Product	Yield (%)
1	C$_6$H$_5$Br	(5a)	2: 48[c]
2	4-CH$_3$C$_6$H$_4$Br	(5b)	1: 40[c,d] 2: 30[c,d] 3: 26[c,d]
3	1-C$_{10}$H$_7$Br	(5c)	1: 85[c]
4	2-OHCC$_6$H$_4$Br	(5d)	1: 89[b] 2: 84[b] 3: 80[b]
5	4-OHCC$_6$H$_4$Br	(5e)	2: 91[b] 2: 97[c]
6	4-CH$_3$COC$_6$H$_4$Br	(5f)	1: 100[b] 2: 97[b] 3: 80[b] 1: 21[d]
7	4-CH$_3$COOC$_6$H$_4$Br	(5g)	1: 83[b] 1: 92[c] 3: 82[c]
8	4-NCC$_6$H$_4$Br	(5h)	1: 89[b] 1: 94[c] 3: 87[c]
9	4-O$_2$NC$_6$H$_4$Br	(5i)	1: 90[b]
10	2-C$_4$H$_3$SBr	(5j)	2: 34[c]
11	4-C$_9$H$_6$NBr	(5k)	2: 77[c]

[a] Reaction conditions: Aryl bromide (1.0 mmol), butyl acrylate (1.5 mmol), NaOAc (1.5 mmol) in H$_2$O, DMA (3 mL), Pd catalyst (0.4 mol% of Pd), 120 °C, 18 h. [b] TBAB (1 mmol) added. [c] TBAB (3 mmol) added. [d] time: 24 h.

However on increasing reaction time from 16 h to 24 h, the yield remains low in the absence of TBAB. The similar reaction with butyl acrylate showed low yield (entry 2, Table 4). All the electron poor aryl bromide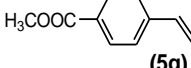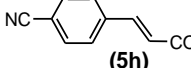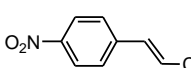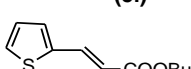 are efficiently coupled with both the alkenes using **1**, **2** and **3** as catalysts to give the corresponding products in very high (> 80%) to quantitative yields. Moreover, the reaction of bromoaldehyde and 4-bromoacetophenone showed excellent coupling with styrene without addition of any TBAB (entry 2-4, Table 3). The coupling of heterocyclic bromides such as 2-bromothiophene and 4-bromoquinoline with both the styrene and butyl acrylate resulted yields of 43, 80% (entry 8-9, Table 3) and 34, 77% (entry 10-11, Table 4) of the corresponding products. The variation (1 mmol or 3 mmol) of TBAB or no TBAB slightly influence the activity of the catalyst and the yields as observed in the experiments of aryl bromides containing functional groups such as methyl ester, cyano, aldehyde, acetyl and nitro groups.

We investigated the low catalyst loading of the complex **1** for both the alkenes with various activated aryl bromides (Table 5) by lowering the concentration by half to 0.2 mol% of Pd, still high yield was maintained with 4-bromoacetophenone and bromoaldehyde. On further lowering the catalyst concentration

to 0.1 or 0.001 times, i.e. molar ratio of substrate / [Pd] ~ 5000, high yield of the products with TON upto 410000 were obtained by the addition of 1 mmol of TBAB (entry 5, Table 5). Under low catalyst loading upto 0.002 mol% of Pd, the reaction of butyl acrylate and 4-bromoacetophenone gave quantitative yields with the addition of 1 mmol of TBAB. Although the yield is dropped to 50% at concentration of 0.0002 mol% of Pd within the same reaction time, the TON raised to 250000 (entry 10-14, Table 5).

As observed in Suzuki-Miyaura cross coupling reactions,[31] the relative catalytic activity of the three palladium complexes follows the trend **1** > **2** > **3** in the present Heck coupling reactions. A slight variation of yield is clearly observed in all the coupling reactions of aryl bromide with both styrene and n-butyl acrylate. The reaction of tolyl bromide and styrene gave the yields of 75, 64 and 59%, whereas the reaction of activated 4-bromoacetophenone with styrene produced 100, 95 and 89% of products as catalyzed by the complexes **1**, **2** and **3**, respectively. The ratios of Pd and dithiolate ligand in all the three macrocyclic complexes are same i.e. 2:1. We have earlier reported that the

Table 5
Effect of catalyst loading on heck reaction[a]

Ar—Br + (alkene) R →[catalyst **1**, 120 °C / DMA, NaOAc] Ar=R

Entry	ArBr	R	Pd mol%	Yield (%)	TON
1	4-CH$_3$COC$_6$H$_4$Br	Ph	0.4	100	250
2	4-CH$_3$COC$_6$H$_4$Br	Ph	0.2	81	405
3	4-CH$_3$COC$_6$H$_4$Br	Ph	0.02	100[b]	5000
4	4-CH$_3$COC$_6$H$_4$Br	Ph	0.002	90[b]	45000
5	4-CH$_3$COC$_6$H$_4$Br	Ph	0.0002	82[b]	410000
6	2-OHCC$_6$H$_4$Br	Ph	0.4	99	248
7	2-OHCC$_6$H$_4$Br	Ph	0.2	92	460
8	4-OHCC$_6$H$_4$Br	Ph	0.4	98	245
9	4-OHCC$_6$H$_4$Br	Ph	0.2	90	450
10	4-CH$_3$COC$_6$H$_4$Br	CO$_2$Bu^n	0.4	100[b]	250
11	4-CH$_3$COC$_6$H$_4$Br	CO$_2$Bu^n	0.2	97[b]	485
12	4-CH$_3$COC$_6$H$_4$Br	CO$_2$Bu^n	0.02	96[b]	4800
13	4-CH$_3$COC$_6$H$_4$Br	CO$_2$Bu^n	0.002	95[b]	47500
14	4-CH$_3$COC$_6$H$_4$Br	CO$_2$Bu^n	0.0002	50[b]	250000
15	1-C$_{10}$H$_7$Br	CO$_2$Bu^n	0.4	85[c]	213
16	1-C$_{10}$H$_7$Br	CO$_2$Bu^n	0.04	31[c]	775

[a] Reaction conditions: Aryl bromide (1.0 mmol), alkene (1.5 mmol), NaOAc in H$_2$O (2 mmol for styrene and 1.5 mmol for butyl acrylate reaction), time (16 hrs for styrene and 18 hrs for butyl acrylate reaction), DMA (3 mL), 120 °C. [b] TBAB (1 mmol) added. [c] TBAB (3 mmol) added.

larger octanuclear complex **3** is more stable than tetranuclear complexes **1** and **2**, as calculated by the DFT computational studies. It may facilitates the formation of catalytically active species slightly more in case of tetranuclear complexes and enhanced the activity. It may be noted that the NCN- or SCS-pincer complexes of lower stability showed higher effective concentrations of catalytically active species than the higher stable PCP-pincer complexes.[1b]

Moreover, experiments were carried out to assess the reusability of the catalyst. After the reaction of styrene and 4-bromoacetophenone, ethyl acetate was added to the product mixture resulting in the formation of two layers. The upper layer of ethyl acetate, containing the product was removed to give 100% yield. The catalyst **1** containing lower aqueous layer was then employed for another reaction, accordingly proportional amount of reactants were further added. After 16 h the first reaction cycle resulted 90% yield, repeating the similar process the second and third reaction cycles yielded 78 and 66% of the products. The results showed that the catalyst remains active with a slight loss of activity after three successive cycles.

In summary, we have demonstrated that the supramolecular palladium dithiolate complexes can catalyse the Heck coupling reactions for a wide range of aryl bromides. These results clearly proves once again that sulfur ligands, can promote C–C bond forming reactions, rather being treated as catalyst poison. A dramatic increase in activities was observed on addition of TBAB. Under optimized conditions and low catalyst loading, the complex can show excellent catalytic activity with high turnover number (TON = 410000) and turnover frequency (TOF = 25625 h^{-1}).

Acknowledgments

Supplementary Data

Experimental procedure for aryl bromide and butyl acrylate, preparation of palladium complexes and spectral data of products are provided in supplementary material.

References and notes

1. (a) Heck, R. F. *Comprehensive Organic Synthesis*, B. M. Trost and I. Fleming (Eds.), Pergamon Press, Oxford, 1991, *vol. 4*, p. 833; (b) Oestreich, M. *The Mizoroki-Heck Reaction*, John Wiley & Sons, 2009.
2. Johansson Seechurn, C. C. C.; Kitching, M. O.; Colacot, T. J.; Snieckus, V. *Angew. Chem. Int. Ed.* **2012**, *51*, 5062–5085.
3. Wolfe, J. P.; Singer, R. A.; Yang, B. H.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 9550–9561.
4. Stambuli, J. P.; Kuwano, R.; Hartwig, J. F. *Angew. Chem. Int. Ed.* **2002**, *41*, 4746–4748.
5. Kim, J. -H.; Kim, J. -W.; Shokouhimehr, M.; Lee, Y. -S. *J. Org. Chem.* **2005**, *70*, 6714–6720.
6. Roland, S.; Mangeney, P.; Jutand, A. *Synlett.* **2006**, 3088–94.
7. Farina, V. *Adv. Synth. Catal.* **2004**, *346*, 1553–1582.
8. Herrera-Alvarez, C.; Gomez-Benitez, G.; Redon, R.; Garcia, J.; Hernandez-Ortega, S.; Toscano, R. A.; Morales-Morales, D. *J. Organomet. Chem.* **2004**, *689*, 2464–72.
9. Chen, W.; Li, R.; Han, B.; Li, B-J.; Chen, Y-C.; Wu, Y.; Ding, L-S. and Yang, D. *Eur. J. Org. Chem.* **2006**, 1177–1184.
10. (a) Paluru, D. K.; Dey, S.; Wadawale, A. and Jain, V. K. *J. Organomet. Chem.,* **2013**, *728*, 52–56; (b) Khairnar, B. J.; Dey, S.; Jain, V. K.; Bhanage, B. M. *Tetrahedron Lett.,* **2014**, *55*, 716–719.; (c) Paluru, D. K.; Dey, S.; Chaudhari, K. R.; Khedkar, M. V.; Bhanage, B. M. and Jain, V. K. *Tetrahedron Lett.,* **2014**, *55*, 2953–2956.
11. Wang, H.; Zhong, R.; Guo, X.-Q.; Feng, X.-Y.; Hou, X.-F. *Eur. J. Inorg. Chem.* **2010** 174–178.
12. Dervisi, A.; Koursarou, D.; Ooi, L-l.; Horton, P. N.; Hurthouse, M. B. *Dalton Trans.* **2006**, 5717–5724.
13. Jones, R. C.; Canty, A. J.; Gardiner, M. G.; Skelton, B. W.; Tolhurst, V-A.; White, A. H. *Inorg. Chim. Acta* **2010**, *363*, 77–87.
14. Singh, P.; Das, D.; Prakash, O.; Singh, A. K. *Inorg. Chim. Acta* **2013**, *394*, 77–84
15. Kostas, I.D.; Steele, B.R.; Terzis, A.; Amosova, S.V.; Martynov, A.V.; Makhaeva, N.A. *Eur. J. Inorg. Chem.* **2006**, 2642–2646.
16. (a) Yuan, D.; Huynh, H. V. *Organometallics* **2010**, *29*, 6020–6027; (b) Fliedel, C.; Braunstein, P. *Organometallics* **2010**, *29*, 5614–5626.
17. Zim, D.; Gruber, A. S.; Ebeling, G.; Dupont, J.; Monteiro, A. L. *Org. Lett.* **2000**, *2*, 2881–2884.
18. Wang, W-C.; Peng, K-F.; Chen, M-T. and Chen, C-T. *Dalton Trans.* **2012**, *41*, 3022–3029.
19. Bergbreiter, D. E.; Osburn, P. L.; Liu, Y. S. *J. Am. Chem. Soc.* **1999**, *121*, 9531.
20. Bai, S-Q. and Andy Hor, T. S. *Chem. Commun.* **2008**, 3172–3174.
21. Yao, Q.; Kinney, E.P.; Zheng, C. *Org. Lett.* **2004**, *6*, 2997–2999.
22. (a) Chakraborty, T.; Srivastava, K.; Singh, H.B.; Butcher, R.J. *J. Organomet. Chem.* **2011,** *696,* 2559–2564; (b) Ghavale, N.; Manjare, S. T.; Singh, H.B.; Butcher, R.J. *Dalton Trans.* **2015**, *44*, 11893–11900.
23. (a) Rao, G.K.; Kumar, A.; Ahmed, J.; Singh, A.K. *Chem. Commun.* **2010**, *46*, 5954–5956; (b) Rao, G.K.; Kumar, A.; Kumar, B.; Kumar, D.; Singh, A.K. *Dalton Trans.* **2012**, *41*, 1931–1937.
24. Vivekananda, K. V.; Dey, S.; Wadawale, A.; Bhuvanesh, N.; Jain, V. K. *Dalton Trans.* **2013**, *42*, 14158–14167.
25. Paluru, D. K.; Dey, S.; Wadawale, A.; Maity, D. K.; Bhuvanesh, N.; Jain, V. K. *Eur. J. Inorg. Chem.* **2015**, 397–407.
26. Dunleavy, J. K. *Platinum Met. Rev.* **2006**, *50*, 110.
27. Vanjari, R.; Guntreddi, T.; Kumar, S.; Singh, K. N. *Chem. Commun.* **2015**, *51*, 366–369.
28. Ananikov, V. P.; Orlov, N. V.; Beletskaya, L. P.; Khrustalev, V. N.; Antipin, M. Yu.; Timofeeva, T. V. *J. Am. Chem. Soc.* **2007**, *129*, 7252–7253.
29. Lu, F.; Ruiz, J. and Astruc, D. *Tetrahedron Lett.* **2004**, 9443–9445.
30. Lu, C. –H. and Chang, F. –C. *ACS Catal.* **2011**, *1*, 481–488.
31. Vivekananda, K. V.; Dey, S.; Maity, D. K.; Bhuvanesh, N.; Jain, V. K. *Inorg. Chem.* **2015**, *54*, 10153–10162.

32. Ooe, M.; Murata, M.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *J. Am. Chem. Soc*. **2004**, *126*, 1604−1605.

33. Yamada, Y. M. A.; Takeda, K.; Takahashi, H.; Ikegami, S. *Tetrahedron Lett*. **2003**, *44*, 2379−2382.

34. Dodds, D. L.; Boele, M. D. K.; van Strijdonck, G.P.F.; de Vries, J. G.; van Leeuwen, P. W. N. M.; Kamer, P. J. *Eur. J. Inorg. Chem*. **2012**, 1660−1671.

35. Kohler, Klaus; Heidenreich, Roland G.; Krauter, Jurgen G. E.; Pietsch, J. *Org, Chem. Eur. J*. **2002**, 8, 622−631.

36. Wang, Furong; Tang, Sisi; Yu, Yinghao; Wang, Lefu; Yin, Biaolin; Li, Xuehui, *Chinese Journal of Catalysis* **2014**, 35, 1921−1926.

37. *Typical experimental procedure*: In an oven dried 25 ml Schlenk tube was charged with DMA (3 mL), aryl bromide (1 mmol), styrene (1.5 mmol), aqueous NaOAc (2 mmol, 1 mL) and catalyst (0.4 mol%). The reactants were heated at 120 ℃ with stirring for 16 h under a nitrogen atmosphere. The reaction mixture was cooled to room temperature, the contents were diluted with water (5 mL), neutralized with dil HCl and extracted with ethyl acetate (3 × 20 mL). The whole organic extract was washed with water (2 × 15 mL), dried over anhydrous Na_2SO_4, filtered and the solvent was removed under reduced pressure. The residue was characterized by NMR spectra.

Research Highlights

➢ Supramolecular palladium thiolate complexes can act as catalysts in Heck reactions.

➢ Arylation of acrylate and styrene was demonstrated under optimized conditions.

➢ Pd complexes showed excellent catalytic activity with high TON (410000).

➢ Tetranuclear complexes showed higher catalytic activity than octanuclear complex.