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Palladium(II)- and platinum(II)-catalyzed addition of stabilized carbon nucleophiles to ethylene and propylene†

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$PdCl_2(CH_3CN)_2$ and $[PtCl_2(H_2C=CH_2)]_2$ catalyze the addition of β-dicarbonyl compounds to ethylene and propylene.

The development of efficient, atom-economical processes for the utilization of readily abundant carbon sources in the production of fine chemicals remains an important challenge in organic synthesis and homogeneous catalysis.[1] Although ethylene and α-olefins represent one of the most important carbon feedstocks employed in the large-scale production of polymers,[2] the direct utilization of ethylene and α-olefins in fine chemical synthesis remains problematic due to the paucity of mild and efficient C–C bond forming transformations applicable to simple olefins.[3] Notable examples include Co- or Rh-catalyzed hydroformylation and hydrocarboxylation,[4] Pd-catalyzed arylation,[5] Ni-catalyzed hydrocyanation,[6] and Ni-catalyzed dimerization[7] and heterodimerization.[1,8] An alternative approach to C–C bond formation that has not been realized is *via* the transition metal-catalyzed addition of a stabilized carbon nucleophile to a simple olefin. Rather, alkylation of unactivated olefins requires employment of either a highly basic, unstabilized carbon nucleophile[9] or a stoichiometric amount of a transition metal complex.[10] Here we report the first examples of the transition metal-catalyzed addition of stabilized carbon nucleophiles to ethylene and propylene.

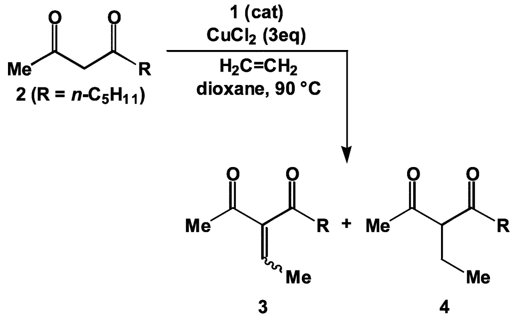
We have recently reported the intramolecular hydroalkylation[11,12] and oxidative alkylation[13] of alkenyl β-diketones and related substrates[14] catalyzed by $PdCl_2(CH_3CN)_2$ (**1**), which represent the first examples of the transition metal-catalyzed addition of a stabilized carbon nucleophile to an unactivated olefin. Given the mild reaction conditions and high regioselectivity of palladium-catalyzed intramolecular olefin alkylation, this system represented a viable starting point for the development of an effective protocol for intermolecular olefin alkylation. In an initial experiment, reaction of 2,4-nonanedione (**2**) with ethylene (1 atm) in the presence of a catalytic amount of **1** (20 mol%) and a stoichiometric amount of $CuCl_2$ at 90 °C for 12 h led to 67% conversion with formation of a 36 : 64 mixture of 3-ethylidene-2,4-nonanedione (**3**) and 3-ethyl-2,4-nonanedione (**4**) (Table 1, entry 1). Both the efficiency and the selectivity of the conversion of **2** to **3** increased with increasing ethylene pressure (Table 1), and palladium-catalyzed reaction of **2** with ethylene (200 psi) led to the exclusive formation of **3** (Table 1, entry 4), which was isolated in 77% yield as a separable mixture of *E* and *Z* isomers (Table 2, entry 1).[‡,§] The enhanced selectivity for **3** relative to **4** at higher ethylene pressure is likely due to the increased rate of associative olefin displacement relative to protonolysis from an equilibrating mixture of palladium olefin hydride and alkyl complexes, respectively.[12]

In addition to **2**, a number of β-dicarbonyl compounds reacted with ethylene in the presence of a catalytic amount of **1** and a stoichiometric amount of $CuCl_2$ to form the corresponding α-ethylidene or α-vinyl β-dicarbonyl compound in good yield (Table 2, entries 2–5). For example, the sterically hindered β-diketone 2,2,6,6-tetramethyl-3,5-heptanedione underwent palladium-catalyzed addition to ethylene to form 2,2,6,6-tetramethyl-4-vinyl-3,5-heptanedione as the exclusive product in 72% isolated yield (Table 2, entry 3). Formation of the α-vinyl β-diketone rather than the α-ethylidene β-diketone is presumably due to unfavorable steric interaction between the ethylidene methyl group and the proximal *tert*-butyl group in the latter isomer. Consistent with this hypothesis, palladium-catalyzed reaction of 5,5-dimethyl-2,4-hexanedione with ethylene formed (*E*)-3-ethylidene-5,5-dimethyl-2,4-hexanedione as the exclusive isomer in 86% isolated yield (Table 1, entry 4). In a similar manner, palladium-catalyzed reaction of ethylene with ethyl 4,4-dimethyl-3-oxopentanoate formed (*Z*)-ethyl 2-(2,2-dimethylpropionyl)-2-butenoate in 59% isolated yield as a single isomer (Table 1, entry 5).

Palladium-catalyzed olefin alkylation was also applicable to propylene, provided that the β-diketone was activated with $EuCl_3$ (Table 2, entries 6 and 7). For example, reaction of 2,6-dimethyl-3,5-heptanedione with propylene (50 psi) in the presence of a catalytic amount of **1** and a stoichiometric mixture of $EuCl_3$ and $CuCl_2$ at 100 °C for 24 h led to the isolation of 3-isopropylidene-2,6-dimethyl-3,5-heptanedione in 51% yield and 3-isobutyryl-2-isopropyl-5-methylfuran in 24% yield (Table 2, entry 6). The furan is presumably formed *via* palladium-catalyzed cyclization of the initially formed 4-allyl-2,6-dimethyl-3,5-heptanedione.[15]

Because selective intermolecular olefin hydroalkylation was not realized employing palladium catalyst **1**, we sought to identify an alternative catalyst for this transformation. Maresca has reported that stabilized carbon nucleophiles react readily with Pt(II)–olefin complexes, and that the resulting platinum alkyl complexes are reactive toward protonolysis but not toward β-hydride elimination.[16] Because these steps constitute a potential catalytic cycle for olefin hydroalkylation,[12] we targeted simple platinum(II) complexes as catalysts for ethylene hydroalkylation. To this end, reaction of **2** with ethylene (50 psi) and a catalytic mixture of $[PtCl_2(H_2C=CH_2)]_2$ (**5**) (2.5 mol%) and HCl (0.2 equiv.) in dioxane at 90 °C for 5 h led to the isolation of **4** in 68% yield without formation of detectable amounts of **3** (Scheme 1).[¶] In addition to **2**,

Table 1 Effect of ethylene pressure on product distribution for the reaction of ethylene with **2** catalyzed by **1**



Entry	Ethylene pressure	Catalyst loading	**3** : **4**[a]	Conversion[a]
1	15 psi	20%	36 : 64	67%
2	45 psi	10%	68 : 32	76%
3	80 psi	10%	89 : 11	90%
4	200 psi	10%	98 : 2	> 95%

[a] Determined by GC analysis *versus* an internal standard.

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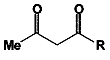
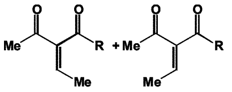
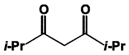
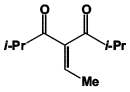
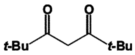
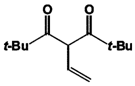
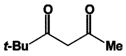
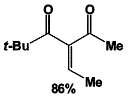
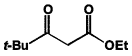
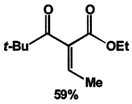
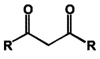
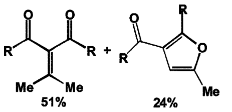
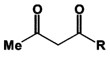
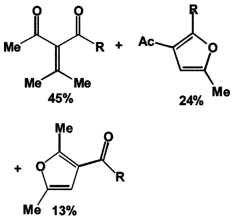
† Electronic supplementary information (ESI) available: experimental procedures, analytical and spectroscopic data for new compounds. See http://www.rsc.org/suppdata/cc/b3/b316734h/

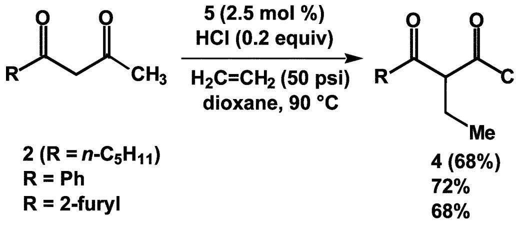
Table 2 Oxidative alkylation of ethylene (200 psi) or propylene (50 psi) with β-dicarbonyl compounds catalyzed by **1** (10 mol%) and $CuCl_2$ (3 equiv.) at 90 °C for 10–24 h

Entry	β-Diketone	Olefin	Product(s)
1	 2 (R = *n*-C_5H_{11})	ethylene	 (*Z*)-3 (45%) (*E*)-3 (32%)
2			 77%
3			 72%
4			 86%
5			 59%
6[a]	 R = *i*-Pr	propylene	 51% 24%
7[a]	 2 (R = *n*-C_5H_{11})		 45% 24% 13%

[a] Reaction run in the presence of $EuCl_3$ (1 equiv.) at 100 °C.

both phenyl- and 2-furyl-substituted β-diketones underwent platinum-catalyzed hydroalkylation with ethylene to form the corresponding α-ethyl β-diketones in good yield (Scheme 1).

In summary, we have presented the first examples of the transition metal-catalyzed addition of stabilized carbon nucleophiles to ethylene and propylene. We are currently working to further expand the scope of these transformations.



Scheme 1

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Notes and references

‡ Turnover numbers for the conversion of **2** to **3** catalyzed by **1** were limited by the use of $CuCl_2$ as the terminal oxidant and not by catalyst decomposition or deactivation. For example, when a suspension of **2** (5 mmol), **1** (0.05 mmol), and $CuCl_2$ (2.0 mmol) was heated under ethylene (200 psi) for 2 h, ~20% of **2** was consumed. When the tube was sparged with O_2, repressurized with ethylene, and heated overnight, an additional ~20% of **2** was consumed. We did not employ catalytic amounts of $CuCl_2$ in these transformations due to safety issues associated with heating pressurized mixtures of ethylene and oxygen.

§ Employment of < 2 equiv. of $CuCl_2$ in the reaction of **2** with ethylene catalyzed by **1** led to incomplete conversion without affecting the **3** : **4** ratio.

¶ Treatment of **2** with ethyl chloride in the presence of $PtCl_2$ (5 mol%) or with HCl (0.2 equiv.) in the absence of platinum led to no detectable consumption of **2** after 5 h at 90 °C.

1 T. V. Rajanbabu, N. Nomura, J. Jin, B. Radetich, H. Park and M. Nandi, *Chem. Eur. J.*, 1999, **5**, 1963.
2 P. A. Arjunan, J. E. McGrath, T. L. Hanlon, Eds., *Olefin Polymerization: Emerging Frontiers*, Oxford University Press, New York, 2000.
3 G. W. Parshall and S. D. Ittel, *Homogeneous Catalysis: The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes*, John Wiley and Sons, New York, 1992.
4 H. M. Colquhoun, D. J. Thompson and M. V. Twigg, *Carbonylation*, Plenum Press, New York, 1991.
5 R. F. Heck, *Org. React.*, 1982, **27**, 345.
6 C. A. Tolman, R. J. McKinney, W. C. Seidel, J. D. Druliner and W. R. Stevens, *Adv. Catal.*, 1985, **33**, 1.
7 Y. Chauvin and H. Olivier, in *Applied Homogeneous Catalysis with Organometallic Compounds* **Vol. 1**, B. Cornils, W. A. Herrmann, Eds., VCH, New York, 1996.
8 Transition metal-catalyzed functionalization of simple olefins *via* C–H bond activation has also been reported: (*a*) F. Kakiuchi and S. Murai, *Acc. Chem. Res.*, 2002, **35**, 826; (*b*) M. Lail, B. N. Arrowood and T. B. Gunnoe, *J. Am. Chem. Soc.*, 2003, **125**, 7506; (*c*) K. L. Tan, R. G. Bergman and J. A. Ellman, *J. Am. Chem. Soc.*, 2002, **124**, 13964.
9 (*a*) H. Pines, *Acc. Chem. Res.*, 1974, **7**, 155; (*b*) U. M. Dzhemilev and O. S. Vostrikova, *J. Organomet. Chem.*, 1985, **285**, 43; (*c*) A. H. Hoveyda and Z. Xu, *J. Am. Chem. Soc.*, 1991, **113**, 5079.
10 T. Hayashi and L. S. Hegedus, *J. Am. Chem. Soc.*, 1977, **99**, 7093.
11 T. Pei and R. A. Widenhoefer, *J. Am. Chem. Soc.*, 2001, **123**, 11290.
12 H. Qian and R. A. Widenhoefer, *J. Am. Chem. Soc.*, 2003, **125**, 2056.
13 T. Pei, X. Wang and R. A. Widenhoefer, *J. Am. Chem. Soc.*, 2003, **125**, 648.
14 (*a*) T. Pei and R. A. Widenhoefer, *Chem. Commun.*, 2002, 650; (*b*) X. Wang, T. Pei, X. Han and R. A. Widenhoefer, *Org. Lett.*, 2003, **5**, 2699.
15 X. Han and R. A. Widenhoefer, *J. Org. Chem.*, in press.
16 F. P. Fanizzi, F. P. Intini, L. Maresca and G. Natile, *J. Chem. Soc., Dalton Trans.*, 1992, 309.