

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

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**$\text{PdCl}_2(\text{CH}_3\text{CN})_2$  and  $[\text{PtCl}_2(\text{H}_2\text{C}=\text{CH}_2)]_2$  catalyze the addition of  $\beta$ -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.<sup>1</sup> Although ethylene and  $\alpha$ -olefins represent one of the most important carbon feedstocks employed in the large-scale production of polymers,<sup>2</sup> the direct utilization of ethylene and  $\alpha$ -olefins in fine chemical synthesis remains problematic due to the paucity of mild and efficient C–C bond forming transformations applicable to simple olefins.<sup>3</sup> Notable examples include Co- or Rh-catalyzed hydroformylation and hydrocarboxylation,<sup>4</sup> Pd-catalyzed arylation,<sup>5</sup> Ni-catalyzed hydrocyanation,<sup>6</sup> and Ni-catalyzed dimerization<sup>7</sup> and heterodimerization.<sup>1,8</sup> 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<sup>9</sup> or a stoichiometric amount of a transition metal complex.<sup>10</sup> 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<sup>11,12</sup> and oxidative alkylation<sup>13</sup> of alkenyl  $\beta$ -diketones and related substrates<sup>14</sup> catalyzed by  $\text{PdCl}_2(\text{CH}_3\text{CN})_2$  (**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  $\text{CuCl}_2$  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.<sup>12</sup>

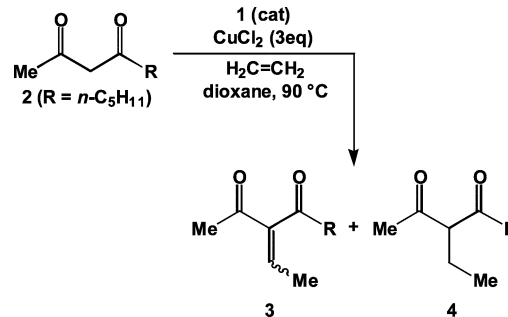
In addition to **2**, a number of  $\beta$ -dicarbonyl compounds reacted with ethylene in the presence of a catalytic amount of **1** and a stoichiometric amount of  $\text{CuCl}_2$  to form the corresponding  $\alpha$ -ethylidene or  $\alpha$ -vinyl  $\beta$ -dicarbonyl compound in good yield (Table 2, entries 2–5). For example, the sterically hindered  $\beta$ -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  $\alpha$ -vinyl  $\beta$ -diketone rather than the  $\alpha$ -ethylidene  $\beta$ -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-butenolate in 59% isolated yield as a single isomer (Table 1, entry 5).

Palladium-catalyzed olefin alkylation was also applicable to propylene, provided that the  $\beta$ -diketone was activated with  $\text{EuCl}_3$  (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  $\text{EuCl}_3$  and  $\text{CuCl}_2$  at 100 °C for 24 h led to the isolation of 3-isopropylidene-2,6-dimethyl-3,5-heptanedione in 51% yield and 3-isobutyl-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.<sup>15</sup>

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  $\beta$ -hydride elimination.<sup>16</sup> Because these steps constitute a potential catalytic cycle for olefin hydroalkylation,<sup>12</sup> 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  $[\text{PtCl}_2(\text{H}_2\text{C}=\text{CH}_2)]_2$  (**5**) (2.5 mol%) and  $\text{HCl}$  (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 <sup>a</sup> | Conversion <sup>a</sup> |
|-------|-------------------|------------------|--------------------|-------------------------|
| 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%                   |

<sup>a</sup> Determined by GC analysis *versus* an internal standard.

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

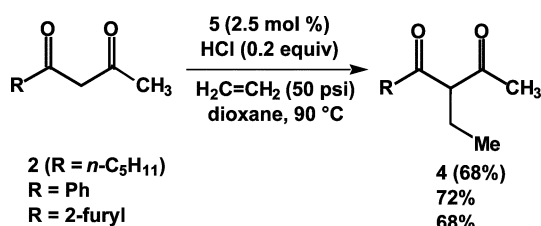
**Table 2** Oxidative alkylation of ethylene (200 psi) or propylene (50 psi) with  $\beta$ -dicarbonyl compounds catalyzed by **1** (10 mol%) and  $\text{CuCl}_2$  (3 equiv.) at 90 °C for 10–24 h

| Entry          | $\beta$ -Diketone | Olefin    | Product(s) |
|----------------|-------------------|-----------|------------|
| 1              |                   | ethylene  |            |
| 2              |                   |           |            |
| 3              |                   |           |            |
| 4              |                   |           |            |
| 5              |                   |           |            |
| 6 <sup>a</sup> |                   | propylene |            |
| 7 <sup>a</sup> |                   |           |            |

<sup>a</sup> Reaction run in the presence of  $\text{EuCl}_3$  (1 equiv.) at 100 °C.

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

In summary, we have presented the first examples of the transition metal-catalyzed addition of stabilized carbon nucleo-



**Scheme 1**

philes to ethylene and propylene. We are currently working to further expand the scope of these transformations.

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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  $\text{CuCl}_2$  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  $\text{CuCl}_2$  (2.0 mmol) was heated under ethylene (200 psi) for 2 h, ~20% of **2** was consumed. When the tube was sparged with  $\text{O}_2$ , repressurized with ethylene, and heated overnight, an additional ~20% of **2** was consumed. We did not employ catalytic amounts of  $\text{CuCl}_2$  in these transformations due to safety issues associated with heating pressurized mixtures of ethylene and oxygen.

§ Employment of < 2 equiv. of  $\text{CuCl}_2$  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  $\text{PtCl}_2$  (5 mol%) or with  $\text{HCl}$  (0.2 equiv.) in the absence of platinum led to no detectable consumption of **2** after 5 h at 90 °C.

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