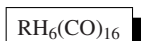


# Hexadecacarbonylhexarhodium<sup>1</sup>



[28407-51-4] C<sub>16</sub>O<sub>16</sub>Rh<sub>6</sub> (MW 1065.62)

InChI = 1/16CO.6Rh/c16\*1-2;;;;;

InChIKey =SZQABOJVTZVBHE-UHFFFAOYAU

(catalyst for hydrogenation of alkenes, hydroformylations of alkenes; reducing agent for aldehydes, ketones, and nitro groups; catalyst for carbenoid reactions of diazo compounds)

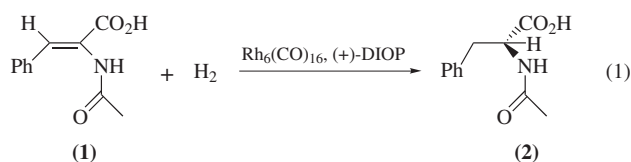
**Physical Data:** mp 235 °C;<sup>2</sup> IR (KBr) CO 2073, 2026, 1800 cm<sup>-1</sup>.<sup>3</sup>

**Solubility:** sol methanol, ethanol, acetone; slightly sol toluene, benzene, hexane.

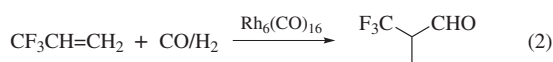
**Form Supplied in:** black crystals.

**Preparative Methods:** from **Rhodium(III) Chloride**<sup>5</sup> or from **Pentacarbonyliron** and RhCl<sub>3</sub>·3H<sub>2</sub>O.<sup>4</sup>

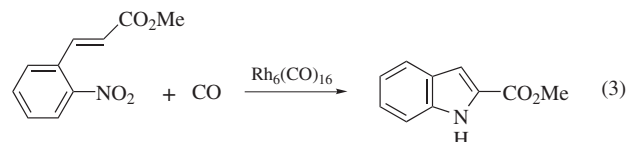
**Catalytic Hydrogenation of Alkenes.** Alkenes are catalytically hydrogenated to alkanes in the presence of Rh<sub>6</sub>(CO)<sub>16</sub>,<sup>5</sup> although the reaction is slow in the absence of a ligand such as **Triphenylphosphine**. Considerable improvement is seen by binding the catalyst to a phosphine-functionalized polystyrene.<sup>6</sup> In the presence of phosphines, Rh<sub>6</sub>(CO)<sub>16</sub> has been found to be a mild, effective catalyst for the hydrogenation of alkenes.<sup>7</sup> Cyclohexene, for example, can be quantitatively reduced to cyclohexane. Asymmetric hydrogenations have been performed in the presence of **(2,3-O-Isopropylidene)-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane** [(+)-DIOP]. *N*-Acylenamine (**1**) was converted to (+)-*N*-acylphenylalanine (**2**) in 40% ee (eq 1) using Rh<sub>6</sub>(CO)<sub>16</sub> and (+)-DIOP.<sup>8</sup> A wide variety of quinolines and isoquinolines have been reduced to 1,2,3,4-tetrahydroquinolines and *N*-formyl 1,2,3,4-tetrahydroisoquinolines in excellent yields under water-gas shift conditions.<sup>9</sup>



**Hydroformylation.** Alkenes undergo hydroformylation to give aldehydes in good yields with Rh<sub>6</sub>(CO)<sub>16</sub> when used as either a homogeneous catalyst or supported on zeolites,<sup>10</sup> to yield mixtures of 'normal' and isoaldehydes.<sup>11</sup> Fluorinated alkenes, however, are hydroformylated with a high degree of selectivity (eq 2), with iso to normal aldehyde ratios of 97:3.<sup>12</sup> Hydroformylations also occur with Rh<sub>6</sub>(CO)<sub>16</sub> under water-gas shift conditions to give mixtures of iso and normal aldehydes,<sup>13</sup> but these conditions have been reported to effect reduction of the resulting aldehydes to alcohols at extended reaction times.<sup>14</sup>

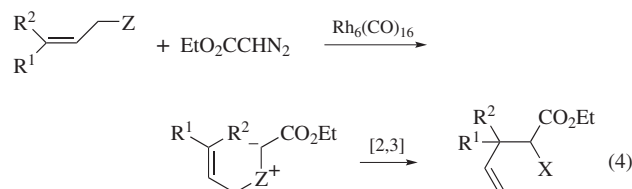


**Reductions of Aldehydes, Ketones, and Aromatic Nitro Groups.** Aldehydes and ketones are reduced under water-gas shift conditions to give alcohols in excellent yields.<sup>15</sup> Aromatic nitro compounds are reduced to anilines under similar conditions.<sup>16</sup> *o*-Nitrostyrenes have been converted to indoles (eq 3) in moderate (68%) yields.<sup>17</sup>



**Reductive Amination.** Primary, secondary, and tertiary amines can be produced in good yield by the reaction of aldehydes and ketones with ammonia or amines in the presence of a catalytic amount of Rh<sub>6</sub>(CO)<sub>16</sub> at 100–300 atm synthesis gas (CO/H<sub>2</sub> = 1:1).<sup>18</sup>

**Metal Carbene Transformations.** Rh<sub>6</sub>(CO)<sub>16</sub> has been found to be an efficient catalyst for dinitrogen extrusion from diazo carbonyl compounds to generate electrophilic metal carbenes that react with allyl sulfides, amines, or iodides to give ylides which undergo [2,3]-sigmatropic rearrangement to form homoallylic sulfides, amines, and iodides (eq 4) in good yield.<sup>19</sup> These carbenes can also react with alkenes to give cyclopropanes in good yields.<sup>20</sup>



**Decarbonylation of Formate Esters.** Formate esters are decarbonylated at 200–220 °C in 2-methoxyethanol in the presence of 1 mol % Rh<sub>6</sub>(CO)<sub>16</sub> to give alcohols in 69–94% yield.<sup>21</sup> The reaction is effective in decarbonylating secondary as well as primary formate esters, producing only small amounts of alkenes as byproducts.

**Related Reagents.** Dirhodium(II) Tetraacetate; Dodecacarbonyltetraheterorhodium; Tetracarbonyl(di-μ-chloro)dirhodium.

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