

61-7; [Et<sub>3</sub>NH][μ-CO](μ-*t*-BuS)Fe<sub>2</sub>(CO)<sub>6</sub>, 105040-77-5; BrC≡C-CH<sub>2</sub>OCH<sub>3</sub>, 54339-94-5; (μ-σ,π-C≡CCH<sub>2</sub>OCH<sub>3</sub>)(μ-*t*-BuS)Fe<sub>2</sub>(CO)<sub>6</sub>, 118576-55-9; (μ,η<sup>1</sup>,η<sup>2</sup>-CH=CHCH=O)(μ-*t*-BuS)Fe<sub>2</sub>(CO)<sub>6</sub>, 118576-56-0; (μ,η<sup>1</sup>,η<sup>2</sup>-PhC=CHCH=O)(μ-EtS)Fe<sub>2</sub>(CO)<sub>6</sub>, 118576-57-1; [Et<sub>3</sub>NH][μ-CO](μ-EtS)Fe<sub>2</sub>(CO)<sub>6</sub>, 93530-38-2; PhC≡CCHO, 2579-22-8; CH<sub>3</sub>O<sub>2</sub>CC=CCO<sub>2</sub>CH<sub>3</sub>, 762-42-5; HC≡CCO<sub>2</sub>CH<sub>3</sub>, 922-67-8; HC≡CC(O)CH<sub>3</sub>, 1423-60-5; CH<sub>3</sub>C≡CCO<sub>2</sub>CH<sub>3</sub>, 23326-27-4.

**Supplementary Material Available:** A table of spectroscopic and analytical data and tables of positional parameters, anisotropic thermal parameters, and bond lengths and angles (16 pages); listings of observed and calculated structure factor amplitudes (62 pages). Ordering information is given on any current masthead page.

## Reactive Mono- and Dinuclear Bis(diphenylphosphino)methane Derivatives of Ruthenium Carbonyls: Ru(CO)<sub>4</sub>(η<sup>1</sup>-dppm) and Ru<sub>2</sub>(CO)<sub>7</sub>(μ-dppm)

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**Summary:** Reaction of bis(diphenylphosphino)methane with in situ generated Ru(CO)<sub>4</sub>(η<sup>2</sup>-CH<sub>2</sub>CHCH<sub>3</sub>) gives Ru(CO)<sub>4</sub>(η<sup>1</sup>-dppm) (**1**). Photolysis of **1** and Ru(CO)<sub>5</sub> or that of Ru<sub>3</sub>(CO)<sub>10</sub>(μ-dppm) in the presence of CO yields Ru<sub>2</sub>(CO)<sub>7</sub>(μ-dppm) (**2**). Evidence for high reactivity of these complexes is presented by the reaction of **2** with CH<sub>2</sub>N<sub>2</sub> and HCCH and that of **1** with [Rh(CO)<sub>2</sub>(solv)<sub>2</sub>]<sup>+</sup> and [Rh(CO)<sub>2</sub>Cl]<sub>2</sub>, all occurring below 0 °C.

Recent investigations by Shaw et al.<sup>1</sup> and Knox et al.<sup>2</sup> have established that Fe(CO)<sub>4</sub>(η<sup>1</sup>-dppm) and Fe<sub>2</sub>(CO)<sub>7</sub>(μ-dppm) (dppm = bis(diphenylphosphino)methane) have a very rich derivative chemistry. The mononuclear iron complex, containing a monodentate diphosphine ligand, is a versatile building block for the synthesis of heterobimetallic complexes while the diiron compound exhibits interesting phosphorus-carbon bond cleavage reactions<sup>2a</sup> and its stepwise reaction with acetylene serves as a realistic model for the iron carbonyl mediated synthesis of tropone. Although the analogous ruthenium derivatives are expected to be even more reactive,<sup>3</sup> their synthesis so far remained elusive. Here we report the successful synthesis of Ru(CO)<sub>4</sub>(η<sup>1</sup>-dppm) (**1**) and Ru<sub>2</sub>(CO)<sub>7</sub>(μ-dppm) (**2**) and divulge some preliminary reactivity studies which bear out these expectations.

In our hands, reaction of dppm with the commonly used "Ru(CO)<sub>4</sub>" transfer reagents such as Ru(CO)<sub>5</sub>,<sup>4a</sup> Ru(CO)<sub>4</sub>(η<sup>2</sup>-C<sub>2</sub>H<sub>4</sub>),<sup>4a</sup> and Ru(CO)<sub>4</sub>(η<sup>2</sup>-CH<sub>2</sub>CHCO<sub>2</sub>CH<sub>3</sub>)<sup>4b</sup> led to mixtures of products with one of the components being **1**. However, successful preparation of **1** was achieved by

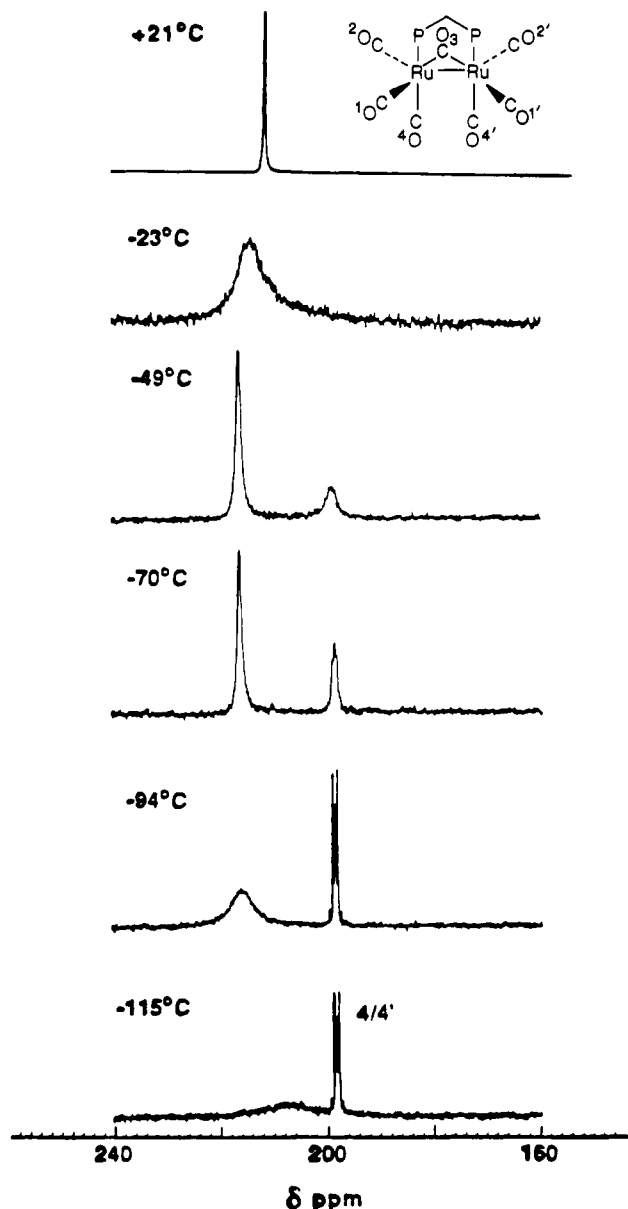
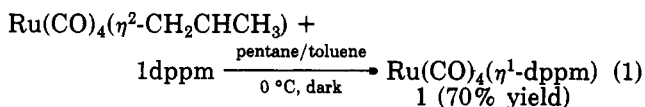
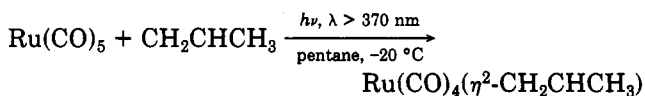


Figure 1. Variable-temperature <sup>13</sup>C NMR spectra of **2**.

the use of the in situ generated, very labile Ru(CO)<sub>4</sub>(η<sup>2</sup>-CH<sub>2</sub>CHCH<sub>3</sub>)<sup>5</sup> (eq 1). Compound **1**<sup>6</sup> is moderately stable



at room temperature, but it must be protected from light since it slowly converts to Ru(CO)<sub>3</sub>(η<sup>2</sup>-dppm). As expected from the behavior of related M(CO)<sub>4</sub>L types of compounds<sup>7</sup>

(1) Fontaine, X. L.; Jacobsen, G. B.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* 1988, 741 and references therein.

(2) (a) Doherty, N. M.; Hogarth, G.; Knox, S. A. R.; Macpherson, K. A.; Melchior, F.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* 1986, 540. (b) Hogarth, G.; Kayser, F.; Knox, S. A. R.; Morton, D. A. V.; Orpen, A. G.; Turner, M. L. *J. Chem. Soc., Chem. Commun.* 1988, 358.

(3) Basolo, F. *Isr. J. Chem.* 1986, 27, 233.

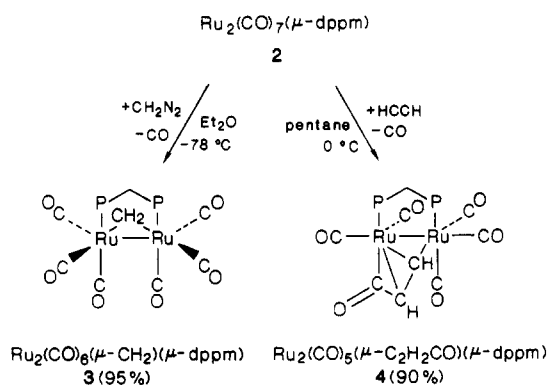
(4) (a) Johnson, B. F. G.; Lewis, J.; Twigg, M. V. *J. Organomet. Chem.* 1974, 67, C75; *J. Chem. Soc., Dalton Trans.* 1975, 1876. (b) Grevels, F.-W.; Reuvers, J. G. A.; Takats, J. *Inorg. Synth.* 1986, 24, 176.

(5) The lability of this compound has so far prevented its isolation. It was identified in solution by IR spectroscopy (cm<sup>-1</sup>, pentane, -20 °C); ν<sub>CO</sub> 2101 w, 2019 vs, 1993 s.

(6) **1**: yellow solid; IR (ν<sub>CO</sub>, pentane, cm<sup>-1</sup>) 2061 s, 1989 m, 1957 s, 1944 s. NMR (δ, ppm, CD<sub>2</sub>Cl<sub>2</sub>): <sup>1</sup>H, 3.33 (dd, CH<sub>2</sub>); <sup>31</sup>P, 38.3 (d, Ru-P), -26.2 (d, free P). Anal. Calcd for C<sub>22</sub>H<sub>22</sub>O<sub>4</sub>P<sub>2</sub>Ru: C, 58.30; H, 3.71. Found: C, 57.60; H, 4.02.

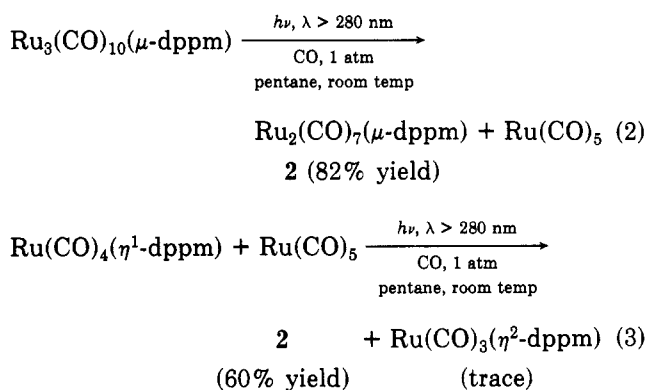
(7) Martin, L. R.; Einstein, W. B.; Pomeroy, R. K. *Inorg. Chem.* 1985, 24, 2777 and references therein.

## Scheme I



(M = Fe, Ru; L = PR<sub>3</sub>), the molecule is fluxional in solution. The single, sharp <sup>13</sup>C NMR signal at 203.8 ppm, due to averaged CO groups, remains unchanged down to -115 °C.

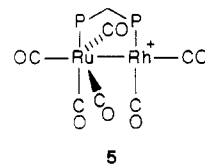
Attempts to convert 1 to the desired diruthenium complex  $\text{Ru}_2(\text{CO})_7(\mu\text{-dppm})$  (2) by thermal reaction with a variety of "Ru(CO)<sub>4</sub>" and "Ru(CO)<sub>3</sub>" transfer reagents were again frustrated by the formation of mixtures, the major component being the known  $\text{Ru}_3(\text{CO})_{10}(\mu\text{-dppm})$ .<sup>8</sup> Synthesis of 2 was achieved by the photochemical routes depicted in eq 2 and 3. The spectral characteristics of 2 are



consistent with its formulation.<sup>9</sup> In accord with the analogous iron derivative,<sup>10</sup> compound 2 is fluxional in solution and exhibits a single averaged carbonyl signal at room temperature. However contrary to the iron complex, the variable-temperature <sup>13</sup>C NMR spectra of compound 2 show distinct and reversible line-shape changes. The appearance of two lines with a 5:2 intensity ratio at -70 °C indicates the stoppage of the local carbonyl scrambling at each ruthenium center at this temperature, while the intermetallic carbonyl group exchange is still rapid and averages the environments of CO ligands 1, 2, 3, 2', and 1'. The latter process also slows down at lower temperatures, but the limiting spectrum has not been reached by -115 °C.

Once isolated in pure form, compound 2 is moderately stable but very reactive in solution (Scheme I). Although the conversion of a bridging CO moiety to a bridging methylene unit is a well-known process,<sup>11</sup> the facility of the reaction here to give 3<sup>12</sup> is nevertheless remarkable. It is also noteworthy that the reaction of acetylene with 2 occurs under mild thermal conditions with the incorporation of one C<sub>2</sub>H<sub>2</sub> unit to give 4<sup>13</sup> exclusively. The reaction of the analogous iron complex requires photochemical initiation and leads to a mixture of compounds, incorporating one, two, and three acetylene units.<sup>2</sup> The thermal stability of both 3 and 4 is greater than that of 2; compound 4 is stable to air.

The high reactivity of the η<sup>1</sup>-dppm complex 1 is evidenced in attempts to build Ru-Rh containing heterobimetallic compounds. As demonstrated by <sup>31</sup>P NMR spectroscopy, 1 reacts with [Rh(CO)<sub>2</sub>(solvent)]<sup>+</sup> and [Rh(CO)<sub>2</sub>Cl]<sub>2</sub> already at -78 °C. Although the former reaction gives stable and well-characterized [(μ-dppm)Ru(CO)<sub>4</sub>Rh(CO)<sub>2</sub>]<sup>+</sup> (5),<sup>14</sup> the course of the latter reaction



appears to be very sensitive to reaction conditions and/or adventitious trace impurities.<sup>15</sup> It is interesting that the analogous reaction between Fe(CO)<sub>4</sub>(η<sup>1</sup>-dppm) and [Rh(CO)<sub>2</sub>Cl]<sub>2</sub> appears to occur without problems and gives, at room temperature, (μ-dppm)Fe(CO)<sub>4</sub>Rh(CO)Cl.<sup>16</sup>

In conclusion, we have demonstrated that by proper combination of starting materials and reaction conditions Ru(CO)<sub>4</sub>(η<sup>1</sup>-dppm) and Ru<sub>2</sub>(CO)<sub>7</sub>(μ-dppm) can be prepared. The high reactivity of the complexes presages rich derivative chemistry which is under investigation as in the synthesis of the analogous alkyl-substituted diphosphine derivatives.

**Acknowledgment.** We thank the Natural Science and Engineering Research Council of Canada and the University of Alberta for financial support.

(11) Hahn, J. E. *Prog. Inorg. Chem.* 1984, 31, 205.

(12) 3: yellow-orange solid; IR (ν<sub>CO</sub>, pentane, cm<sup>-1</sup>) 2060 s, 2023 s, 1993 s, 1974 sh, 1965 s, 1958 m. NMR (δ, ppm, CD<sub>2</sub>Cl<sub>2</sub>): <sup>1</sup>H, 5.20 (dt, 1 H, μ-CH<sub>2</sub>), 4.16 (dt, 1 H, μ-CH<sub>2</sub>), 3.81 (dt, 1 H, CH<sub>2</sub>), 3.20 (dt, 1 H, CH<sub>2</sub>); <sup>13</sup>C, 201.7 (t, CO), 72.8 (br, μ-CH<sub>2</sub>), 30.1 (t, CH<sub>2</sub>); <sup>31</sup>P, 32.5 (s). Anal. Calcd for C<sub>37</sub>H<sub>36</sub>O<sub>6</sub>P<sub>2</sub>Ru<sub>2</sub>: C, 52.87; H, 4.32. Found: C, 52.85; H, 4.60.

(13) 4: yellow solid; IR (ν<sub>CO</sub>, CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>) 2061 s, 1993 vs, 1976 sh, 1939 m, 1703 m. NMR (δ, ppm, CD<sub>2</sub>Cl<sub>2</sub>): <sup>1</sup>H (-40 °C), 8.19 (dd, 1 H, μ-COC<sub>2</sub>H<sub>2</sub>), 4.59 (dd, 1 H, μ-COC<sub>2</sub>H<sub>2</sub>), 4.11 (dt, 1 H, CH<sub>2</sub>), 2.85 (dt, 1 H, CH<sub>2</sub>); <sup>13</sup>C (-49 °C), 233.7 (d, μ-COC<sub>2</sub>H<sub>2</sub>), [207.1 (s), 200.6 (d), 199.0 (d), 197.3 (d), 194.1 (d) (CO)], 161.9 (br, Ru-CHCHCO), 55.4 (m, Ru-CHCHCO), 40.4 (t, CH<sub>2</sub>); <sup>31</sup>P, 30.3 (d), 44.2 (d). Anal. Calcd for C<sub>33</sub>H<sub>24</sub>O<sub>6</sub>P<sub>2</sub>Ru<sub>2</sub>: C, 50.77; H, 3.10. Found: C, 51.19; H, 3.19.

(14) 5: red solid; IR (ν<sub>CO</sub>, CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>) 2110 s, 2073 s, 2044 sh, 2023 s, 2012 s. NMR (δ, ppm, CD<sub>2</sub>Cl<sub>2</sub>): <sup>13</sup>C (-94 °C), [195.9 (d), 192.4 (d), 185.8 (d) (Ru-CO)], [190.0 (dd), 176.9 (dd) (Rh-CO)]; <sup>31</sup>P, 28.3 (d), 24.6 (dd). Anal. Calcd for C<sub>36</sub>H<sub>30</sub>O<sub>10</sub>P<sub>2</sub>F<sub>3</sub>SRhRu: C, 44.23; H, 3.09. Found: C, 44.42; H, 3.06 [(μ-dppm)Ru(CO)<sub>4</sub>Rh(CO)<sub>2</sub>THF]CF<sub>3</sub>SO<sub>3</sub>.

(15) The first step in this reaction is undoubtedly simple addition of 1 to the rhodium compound resulting in the formation of (μ-dppm)Ru(CO)<sub>4</sub>Rh(CO)<sub>2</sub>Cl. Indeed treatment of the reaction mixture at low temperature with AgBF<sub>4</sub> gives a complex analogous to 5. Subsequent steps in the reaction are presently unclear. Warming the reaction mixture in the absence of AgBF<sub>4</sub> gives variable results and so far uncharacterized products.

(16) Jacobsen, G. B.; Shaw, B. L.; Thornton-Pett, M. J. *Chem. Soc., Dalton Trans.* 1987, 2751.

(8) (a) Cotton, F. A.; Hanson, B. E. *Inorg. Chem.* 1977, 16, 3369. (b) Bruce, M. I.; Matison, J. G.; Nicholson, B. K. *J. Organomet. Chem.* 1983, 247, 321.

(9) 2: yellow solid; IR (ν<sub>CO</sub>, pentane, cm<sup>-1</sup>) 2062 vs, 2020 s, 1996 s, 1970 m, 1962 s, 1945 m, 1762 m. NMR (δ, ppm, CD<sub>2</sub>Cl<sub>2</sub>): <sup>1</sup>H, 3.57 (t, CH<sub>2</sub>); <sup>31</sup>P, 35.3 (s). Anal. Calcd for C<sub>32</sub>H<sub>22</sub>O<sub>7</sub>PRu<sub>2</sub>: C, 51.14; H, 2.95. Found: C, 51.30; H, 3.54.

(10) Cotton, F. A.; Troup, J. M. *J. Am. Chem. Soc.* 1974, 96, 4422.