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Communications

Binuclear Alkyl Complexes: Unusual Ethylene Adducts and Facile C–H Activation of a Methyl Group by an Adjacent Metal

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Summary: The reactions of [$MIr(CO)_3(dppm)_2$] (M = Rh, Ir; dppm = $Ph_2PCH_2PPh_2$) with methyl triflate yield [$RhIr(CH_3)(CO)_3(dppm)_2$][CF_3SO_3] and the unusual product of C–H activation of a methyl group [$Ir_2H(CO)_3(\mu$-$CH_2)(dppm)_2$][CF_3SO_3], respectively. The reactivities of these species with small molecules such as H_2, CO, C_2H_4, and PR_3 are reported.

Alkyl complexes of the Co-triad metals are known to be involved as key intermediates in a variety of important catalytic processes such as the carbonylation of methanol,[1] the hydrogenation of carbon monoxide,[2] and olefin hydrogenation, hydroformylation, and hydrosilation.[3] Although work on mononuclear alkyl complexes of these metals has resulted in an improved understanding of the involvement of the metal alkyl species in catalysis,[4] very little has been reported on binuclear derivatives, in spite of recent interest in utilizing complexes containing adjacent metals as catalysts.[5]

We have previously reported two unusual, binuclear alkyl complexes involving Rh and Ir, [$MRe(CH_3)(CO)_4$-$(dppm)_2$][CF_3SO_3] (M = Rh, Ir), in which the alkyl group is bound to the group 9 metal, and have described some of the transformations involving these groups.[6] More recently a series of related alkyl compounds involving the Rh/Os[7] and Rh/Mn[8] combinations of metals have also been characterized and studied. In this report we describe the alkylation of the complexes [$MIr(CO)_3(dppm)_2$] (M = Rh, Ir; dppm = $Ph_2PCH_2PPh_2$) and some of the unusual transformations that occur, including the very facile, reversible C–H activation of a coordinated methyl group by an adjacent metal.

The reaction of [$RhIr(CO)_3(dppm)_2$] (**1**) with 1 equiv of methyl triflate yields the methyl complex [$RhIr(CH_3)$-$(CO)_3(dppm)_2$][CF_3SO_3] (**2**),[9] having the methyl group terminally bound to Ir. This is unlike the analogous alkyl complexes of Rh/Re,[6] Rh/Os,[7] and Rh/Mn,[8] all of which have the alkyl groups bound to Rh. The ^1H NMR spectrum of **2** shows the methyl resonance as a triplet at δ −0.08, and selective ^{31}P-decoupling experiments confirm that the methyl protons are coupled only to the phosphorus nuclei on Ir. The $^{13}C\{^1H\}$ NMR spectrum of a ^{13}CO-enriched sample also confirms the structure of **2**, having only one carbonyl on Rh and two on Ir. Preliminary results on the reactivity of **2** are summarized in Scheme I. Reaction of **2** with H_2 yields the known trihydride species **3**,[10] through methane and CO evolution. Although no methyl hydride intermediate was observed

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(1) Foster, D. *Adv. Organomet. Chem.* **1979**, *17*, 255.

(2) Dombek, B. D. *Adv. Catal.* **1983**, *32*, 325.

(3) (a) James, B. R. *Adv. Organomet. Chem.* **1979**, *17*, 319. (b) Pruet, R. L. *Adv. Organomet. Chem.* **1979**, *17*, 1. (c) Masters, C. *Homogeneous Transition-Metal Catalysis: A Gentle Art*; Chapman and Hall: London, 1980. (d) Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407.

(4) (a) Parshall, G. W.; Mrowca, J. J. *Adv. Organomet. Chem.* **1968**, *7*, 157. (b) Atwood, J. D. *Coord. Chem. Rev.* **1988**, *83*, 93.

(5) (a) Balch, A. L. In *Homogeneous Catalysis with Metal Phosphine Complexes*; Pignolet, L. H., Ed.; Plenum: New York, 1983. (b) Brown, M. P.; Fisher, J. R.; Franklin, S. J.; Puddephatt, R. J.; Thomson, M. A. In *Catalytic Aspects of Metal Phosphine Complexes*; Alyea, E. C., Meek, D. W., Eds.; Advances in Chemistry Series 196; American Chemical Society: Washington, DC, 1982; p 231. (c) Poilblanc, R. *Inorg. Chim. Acta* **1982**, *62*, 75. (d) Muetterties, E. L.; Krause, M. J. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 135. (e) Ertl, G. In *Metal Clusters in Catalysis*; Gates, B. C., Guczi, L., Knozinger, H., Eds.; Elsevier: New York, 1986; Chapter 11. (f) Levigne, G.; Kaesz, H. D. In ref 5e, Chapter 4. (g) Marko, L.; Vizi-Orosz, A. In ref 5e, Chapter 5.

(6) Antonelli, D. M.; Cowie, M. *Organometallics* **1991**, *10*, 2550.

(7) Moro, G.; Hilts, R. W.; Sterenberg, B. T.; Cowie, M., manuscript in preparation.

(8) Wang, L.-S.; Cowie, M., to be submitted for publication.

(9) Data for **2** (light brown powder): $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −40 °C) δ 29.84 (dm, $^1J_{Rh-P}$ = 120 Hz), −5.50 (m); ^1H NMR (CD_2Cl_2, −40 °C) δ 4.33 (m, 4 H), −0.08 (t, 3 H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −40 °C) δ 183.72 (dt, 1 C, $^1J_{Rh-C}$ = 75 Hz), 187.9 (bm, 2 C) (all ^{13}C NMR studies on ^{13}CO-enriched samples); IR (Nujol mull) ν(CO) 1986, 1971, 1912 cm^{-1}. Anal. Calcd for $RhIrSF_3P_4O_6C_{55}H_{47}$: C, 50.35; H, 3.61. Found: C, 50.17; H, 3.83.

(10) McDonald, R.; Cowie, M. *Inorg. Chem.* **1990**, *29*, 1564.

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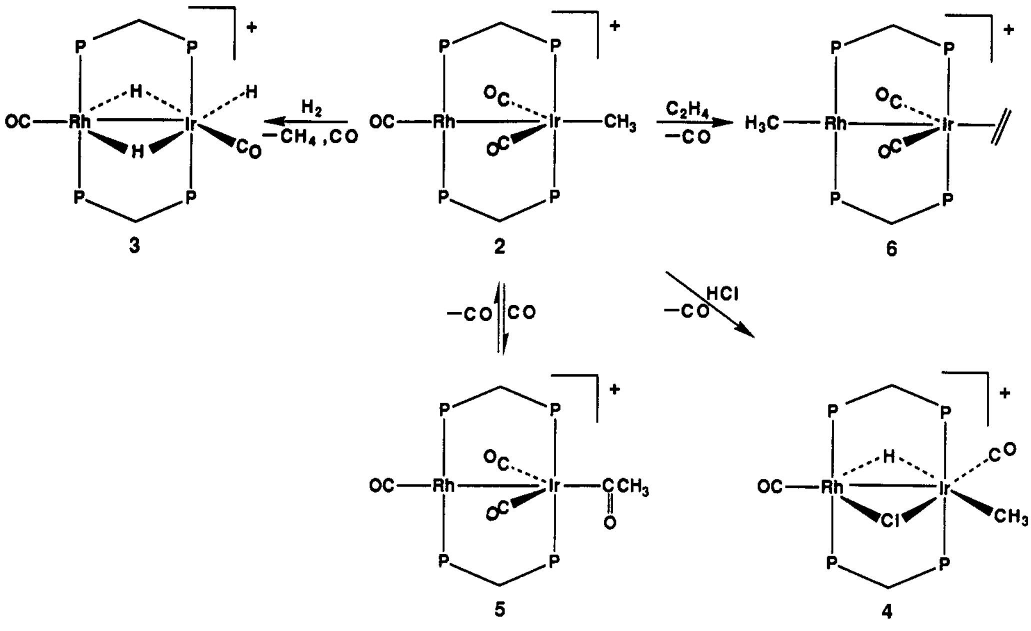
Scheme I



in this reaction, such a species is obtained in the reaction of 2 with 1 equiv of HCl to give $[RhIr(CH_3)(CO)_2(\mu\text{-}H)(\mu\text{-}Cl)(dppm)_2][CF_3SO_3]$ (4).[11] Compound 4 represents a rare example in which a hydrido–methyl complex is stable to methane elimination. Although the relative positions of the equatorial ligands are not known, it is assumed that the hydride and methyl groups are trans, inhibiting reductive elimination. The hydride ligand is clearly bridging, and the methyl group remains coordinated to iridium, as demonstrated by the appropriate NMR experiments. Reaction of 2 with CO yields the acyl complex 5,[12] which is analogous to the methyl precursor; the acyl stretch in the IR spectrum of 5 appears at 1623 cm^{-1}, and the ^{13}C NMR resonance for the acyl carbon is observed at δ 227.9. Possibly the most unusual reaction of 2 involves its incorporation of ethylene to yield $[RhIr(CH_3)(CO)_2(C_2H_4)(dppm)_2][CF_3SO_3]$ (6).[13] The migration of the methyl group to Rh has yielded a compound which is analogous to $[RhOs(CH_3)(CO)_3(dppm)_2]$, which also has the methyl group on Rh and has three carbonyls on Os.[7] The ethylene and methyl protons of 6 appear as triplets at δ 0.75 and 0.35, respectively, in the ^1H NMR spectrum, and although neither resonance displays resolvable coupling to Rh, selective ^{31}P-decoupling experiments confirm that the ethylene protons are coupled to the Ir-bound phosphorus nuclei whereas the methyl protons are coupled to the phosphorus nuclei on Rh. The absence of observable Rh coupling in the methyl signal is not unexpected, since in related species this coupling has been shown to be quite small (2–3 Hz),[6,7] and the broad triplet for the methyl group in 6 could easily mask such coupling. Both carbonyls are semibridging, as shown by the ^{13}C NMR spectrum in which coupling to Rh of 20 Hz is observed.[14] Ethylene adducts of dppm-bridged binuclear complexes of Rh or Ir are extremely rare (to our knowledge $[Ir_2(CO)(C_2H_4)(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][X]$ (X = I, BF_4) are the only other examples);[15] thus compound 6 having an accompanying alkyl group is unprecedented.

Replacing the Rh atom in 1 by the more basic Ir atom, to give $[Ir_2(CO)_3(dppm)_2]$ (7), results in a dramatic change in reactivity upon alkylation. The reaction of 7 with methyl triflate in CH_2Cl_2 at 0 °C gives two characterizable species in a 1.2:1 ratio, together with unidentified decomposition products. The major species $[Ir_2H(CO)_3(\mu\text{-}CH_2)(dppm)_2][CF_3SO_3]$ (8),[16] is the novel hydrido, methylene-bridged species shown in Scheme II. Selective and broad-band ^{31}P-decoupling experiments clearly differentiate the two methylene resonances of the dppm groups from that bridging the metals (δ 4.60). This latter resonance appears as an apparent quintet in the ^{31}P-coupled ^1H NMR spectrum and simplifies to a triplet upon selectively decoupling *either* ^{31}P resonance and to a singlet upon broad-band ^{31}P decoupling, whereas the dppm methylene protons appear as the expected AB quartet (at δ 5.28, 3.59) upon ^{31}P-broad-band decoupling. Although the chemical shift for the dimetalated methylene protons is slightly outside the wide range quoted for such groups when they bridge a metal–metal bond (δ 5–11),[17] the significance of this observation is not clear, since we are aware of at least two reports in which methylene protons in related species

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(11) Data for 4 (orange powder): $^{31}P\{^1H\}$ NMR (CD_2Cl_2, room temperature) δ 22.13 (dm, $^1J_{Rh-P}$ = 111 Hz), −4.39 (m); ^1H NMR (CD_2Cl_2, room temperature) δ 4.4 (m, 2 H), 3.83 (m, 2 H), −0.25 (t, 3 H), −9.5 (m, 1 H, $^1J_{Rh-H}$ = 20 Hz); $^{13}C\{^1H\}$ NMR (CD_2Cl_2; room temperature) δ 189.33 (dt, 1 C, $^1J_{Rh-C}$ = 84.5 Hz), 164.35 (t, 1 C); IR (Nujol mull) ν(CO) 1982, 1932 cm^{-1}. Anal. Calcd for $RhIrClSF_3P_4O_5C_{54}H_{48}$: C, 49.12; H, 3.66; Cl, 2.68. Found: C, 48.38; H, 3.43; Cl, 3.93. Analytical results are variable owing to loss of the CH_2Cl_2 of crystallization. The above results, obtained over a short time span, agree very well with the calculated values if $^1/_4$ equiv of CH_2Cl_2 is assumed (calcd: C, 48.56; H, 3.64; Cl, 3.96).

(12) Data for 5 (light yellow solution; solid not isolated): $^{31}P\{^1H\}$ NMR (CD_2Cl_2, room temperature) δ 26.73 (dt, J_{Rh-P} = 128.7 Hz), 45.79 (t); ^1H NMR (CD_2Cl_2, room temperature) δ 3.60 (bs, 4 H), 0.83 (bs, 3 H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, room temperature) δ 227.87 (bs, 1 C), 194.50 (m, 2 C), 187.87 (m, 1 C); IR (CH_2Cl_2) ν(CO) 2003, 1980, 1623 cm^{-1}.

(13) Data for 6 (orange solution): $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −40 °C) δ 32.58 (dm, $^1J_{Rh-P}$ = 141.1 Hz), 5.38 (m); ^1H NMR (CD_2Cl_2, −40 °C) δ 3.32 (m, 4 H), 0.75 (t, 4 H), 0.35 (t, 3 H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −40 °C) δ 204.74 (dm, 2 C, $^1J_{Rh-C}$ = 20 Hz); IR (CH_2Cl_2) ν(CO) 1985 cm^{-1}.

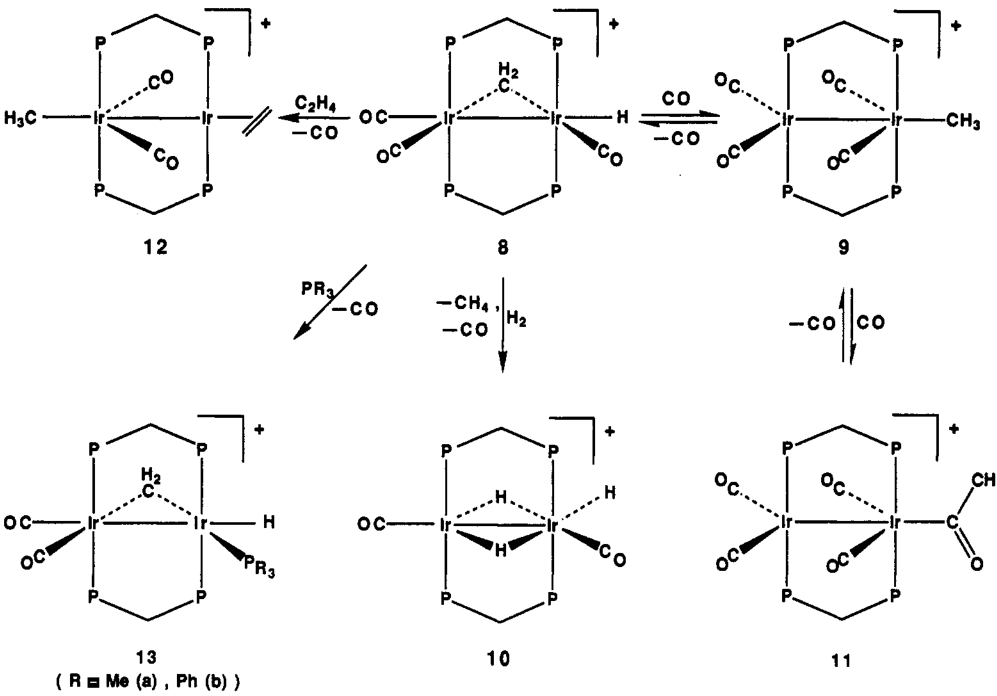
(14) Terminal carbonyls on Rh generally show coupling to Rh of ca. 60–70 Hz, and symmetrically bridging carbonyls display coupling of ca. 30 Hz. The observed coupling of 20 Hz suggests a weaker interaction with Rh.

(15) Vaartstra, B. A.; Xiao, J.; Jenkins, J. A.; Verhagen, R.; Cowie, M. *Organometallics* 1991, *10*, 2708.

(16) Data for 8 (light brown powder): $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −60 °C) δ −0.34 (t), −12.61 (t); ^1H NMR (CD_2Cl_2, −60 °C) δ 5.28 (m, 2 H), 4.60 (m, 2 H), 3.59 (m, 2 H), −11.25 (t, 1 H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −60 °C) δ 177.4 (t, 1 C), 177.0 (t, 1 C), 162.0 (t, 1 C); IR (Nujol mull) ν(CO) 2018, 2000, 1970 cm^{-1}. Anal. Calcd for $Ir_2SF_3P_4O_6C_{55}H_{47}$: C, 47.2; H, 3.37. Found: C, 47.32; H, 3.40.

(17) (a) Herrmann, W. A. *Adv. Organomet. Chem.* 1982, *20*, 159. (b) Puddephatt, R. J. *Polyhedron* 1988, *7*, 767.

Scheme II



resonate at even higher field (δ 4.32, 4.78, 4.08)[18] than for 8. Unfortunately we have not yet succeeded in identifying the ^{13}C resonance of the methylene group in samples prepared using nonenriched methyl triflate. Compound 8 is the unusual result of C–H activation of a coordinated methyl group by an adjacent metal center—a transformation that has only rarely been observed.[18a,19] In addition, it appears that this reversible transformation is unusually facile. At ambient temperature the ^1H resonances of the bridging methylene and hydride ligands are broad and unresolved, suggesting an exchange between the two, presumably via an intermediate methyl complex. This exchange has been confirmed by a spin-saturation-transfer experiment at −30 °C, in which saturation of one signal causes a corresponding decrease in the intensity of the other. The other product observed in the preparation of 8, namely $[Ir_2(CH_3)(CO)_4(dppm)_2][CF_3SO_3]$ (9),[20] is the result of CO addition to either 8 or the methyl intermediate, with the source of CO presumably being the unidentified decomposition products. Compounds 8 and 9 are readily interconvertible at room temperature by the addition or removal of CO. The transformations involving 8 are not unlike those of 2; thus, under H_2 the known trihydride 10[21] is obtained and under CO the labile acyl complex 11 is identified.[22] Reaction of 8 with ethylene yields $[Ir_2(CH_3)(CO)_2(C_2H_4)(dppm)_2][CF_3SO_3]$ (12), another unusual methyl–ethylene complex.[23] It is perhaps surprising that substitution of one CO by C_2H_4 has resulted in hydride migration to the methylene group; thus, although compounds 8 and 12 are isoelectronic, the former is a hydrido–methylene complex, whereas 12 is a methyl species. An interesting difference between 12 and its mixed-metal Rh/Ir analogue 6 is that in 12 the carbonyls are attached to the metal bearing the methyl group, whereas in 6 the carbonyls and ethylene ligands are attached to the same metal. As such, compound 12 actually resembles the Rh/Ir methyl complex 2, having the methyl group on the saturated metal.

The facile and reversible hydride migration to the methylene group to give a methyl ligand, as observed upon CO addition, is not observed upon addition of phosphines. Instead, the phosphine-substitution products $[Ir_2H(CO)_2(PR_3)(\mu\text{-}CH_2)(dppm)_2][CF_3SO_3]$ (R = Me (**13a**), Ph (**13b**)) are obtained.[24] It is interesting to note that the dimetalated methylene protons of **13a** and **13b** resonate at even higher field than in 8 (δ 3.05 (**13a**), 3.71 (**13b**)). In addition, **13a** differs from 8 in that no exchange between the hydride ligand and the methylene protons is observed at 20 °C (by spin-saturation-transfer experiments). This trend is in line with the expected stabilization of the oxidative-addition product (the hydrido–methylene species) by the more electron-donating PMe_3 group. Although the reactions of 8 with phosphines differ from those involving CO and C_2H_4 (see Scheme II), it is suggested that all proceed through the same coordinatively unsaturated methyl intermediate formed in the facile and reversible

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(18) (a) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* 1977, *99*, 5225. (b) Chetcuti, M. J.; Grant, B. E. *Organometallics* 1990, *9*, 1345.

(19) See for example: (a) Park, J. W.; Mackenzie, P. B.; Schaefer, W. P.; Grubbs, R. H. *J. Am. Chem. Soc.* 1986, *108*, 6402. (b) Kulzick, M. A.; Price, R. T.; Andersen, R. A.; Muetterties, E. L. *J. Organomet. Chem.* 1987, *333*, 105. (c) Jacobsen, E. N.; Goldberg, K. I.; Bergman, R. G. *J. Am. Chem. Soc.* 1988, *110*, 3706. (d) Hostetler, M. J.; Bergman, R. G. *J. Am. Chem. Soc.* 1990, *112*, 8621.

(20) Data for 9: $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −60 °C) δ −8.87 (m), −16.0 (m); ^1H NMR (CD_2Cl_2, −60 °C) δ 4.59 (m, 4 H), 0.38 (t, 3 H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −60 °C) δ 194.19 (bs, 2 C), 182.93 (t, 2 C).

(21) McDonald, R.; Sutherland, B. R.; Cowie, M. *Inorg. Chem.* 1987, *26*, 3333.

(22) Data for 11 (light yellow solution): $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −40 °C) δ −9.6 (m), −25.5 (m); ^1H NMR (CD_2Cl_2, −40 °C) δ 4.61 (bs, 4 H), 0.63 (s, 3 H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, room temperature) δ 225.14 (t, 1 C), 195.57 (bs, 2 C), 179.9 (t, 2 C); IR (CH_2Cl_2) ν(CO) 2049, 1959, 1622 cm^{-1}.

(23) Data for 12 (red solution): $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −40 °C) δ 18.95 (m), 5.66 (m); ^1H NMR (CD_2Cl_2, −40 °C) δ 3.25 (m, 4 H), 1.05 (t, 4 H), 0.7 (t, 3 H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −40 °C) δ 204.03 (t, 2 C).

(24) Data for **13a** (light yellow microcrystalline solid): $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −40 °C) δ −7.65 (m), −11.25 (m), −79.24 (bs); ^1H NMR (CD_2Cl_2, −40 °C) δ 4.05 (m, 2 H), 3.45 (m, 2 H), 3.05 (m, 2 H), 0.75 (d, 9 H), −12.35 (dt, 1 H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −40 °C) δ 182.99 (t, 1 C), 180.1 (bs, 1 C); IR (Nujol mull) ν(CO) 2068, 1961, 1950, 1911 cm^{-1}. Anal. Calcd for $Ir_2SF_3P_5O_5C_{57}H_{56}$: C, 47.23; H, 3.89. Found: C, 47.12; H, 4.12. Data for **13b** (orange solid): $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −40 °C) δ −4.06 (m), −13.74 (m), −33.93 (bs); ^1H NMR (CD_2Cl_2, −40 °C) δ 3.84 (m, 2 H), 3.71 (m, 2 H), 3.13 (m, 2 H), −13.25 (dt, 1 H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −40 °C) δ 183.35 (t, 1 C), 180.51 (s, 1 C); IR (Nujol mull) ν(CO) 1975, 1948 cm^{-1}. Microanalysis was not done since **13b** is always contaminated with ca. 20% starting material, 8.

hydrido–methylene-to-methyl transformation that was noted earlier for compound 8. These "RhIr" and "Ir_2" systems described offer a unique opportunity for the investigation of the stepwise transformations involved in the activation of an alkyl C–H bond by an adjacent metal. By varying the ancillary ligands, it should be possible to "fine tune" the electron density at the metals such that the transformation from terminal methyl to bridged methyl to hydrido–methylene species can be effected.

Binuclear complexes in which facile and reversible methyl-to-hydrido–methylene interconversions occur in the presence of unsaturated substrates, such as ethylene, are of obvious importance in studies involving the coupling of organic substrates. Such coupling may occur via alkyl migration to the olefin ligand,[25] by insertion of the olefin into a bridging methylene group,[26] or by olefin insertion into the metal–hydride bond to give a methylene-bridged alkyl complex,[19d] which may then undergo coupling of the alkyl and methylene moieties. It is hoped that future studies on these systems will yield information about these important processes.

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Registry No. **1**, 126501-61-9; **2**, 143171-99-7; **3**, 143172-00-3; **4**, 143172-02-5; **5**, 143172-04-7; **6**, 143172-06-9; **7**, 97487-41-7; **8**, 143172-08-1; **9**, 143172-10-5; **10**, 143172-11-6; **11**, 143172-13-8; **12**, 143172-15-0; **13a**, 143172-17-2; **13b**, 143172-19-4.

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(25) See for example: (a) Flood, T. C.; Bitler, S. P. *J. Am. Chem. Soc.* **1984**, *106*, 6076. (b) Watson, P. L. *J. Am. Chem. Soc.* **1982**, *104*, 337. (c) Evitt, E. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 3973.

(26) (a) Summer, C. E., Jr.; Riley, P. E.; Davis, R. E.; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 1752. (b) Motyl, K. M.; Norton, J. R.; Schauer, C. K.; Anderson, O. P. *J. Am. Chem. Soc.* **1982**, *104*, 7325.

Tailored Synthesis of Hydrocarbon Chains via C–C Coupling Reactions of Diynes and Alkynes on the Square Face of an Ru_4P Cluster

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Summary: The mixed transition-metal–main-group cluster $Ru_4(\mu_3\text{-}PPh)(CO)_{13}$ (1) trimerizes diynes and codimerizes alkynes and diynes to form novel 12- and 8-carbon-atom hydrocarbyls. The X-ray structures of $Ru_4(CO)_8(\mu_4\text{-}PPh)[\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}(Ph)CC(C{\equiv}CPh)C(Ph)C\text{-}\eta^4\text{-}CC(Ph)C(Ph)C(C{\equiv}CPh)]$ (**2**) and $Ru_4(CO)_{10}(\mu\text{-}CO)_2[\mu_4\text{-}\eta^1(P){:}\eta^1(P){:}\eta^1(P){:}\eta^1(C){:}\eta^2(C)\text{-}P(Ph)C(C{\equiv}CPh)C(Ph)]$ (**3**) are reported.

Carbon–carbon bond-forming reactions in di-[1] and polynuclear[2] clusters are of considerable current interest because of their potential for generating new and unusual types of linked hydrocarbon rings and chains. Such reactions may also serve as models for related processes occurring on metal surfaces.[3] Although there are many examples of novel reactivity patterns for alkynes coordinated in a multisite fashion at polynuclear metal centers, there are surprisingly few reports of diyne oligomerization at a cluster surface.[2a,4] An example of the synthesis of a diyne from an acetylide precursor has recently been described.[5] In this communication we report two new results: (i) the unprecedented coupling of three diynes to produce a 12-carbon hydrocarbyl fragment and (ii) the cocoupling of diynes and alkynes to afford novel co-oligomers with variable hydrocarbon chain lengths. While coupling of alkynes with μ_3 or μ_2 group 15 and 16 cluster stabilizing atoms to give novel M_nXC_2 (X = S, P, N) metallacycles is well established,[6] we are unaware of any examples of diyne or diyne–yne oligomerization via the intermediacy of $\mu_3\text{-}\eta^2\text{-}\parallel$ (M_2P) yne coordination and P–C bond making and breaking on a phosphinidene cluster.

We have investigated the reactivity of the 62-electron butterfly or nido cluster $Ru_4(CO)_{13}(\mu_3\text{-}PPh)$[7] (1) toward a variety of diyne ligands and observed facile P–C bond formation/cleavage reactions and framework rearrangements in which the phosphorus atom appears to adopt the role of a skeletal atom. Thus, a solution of 1 in *n*-hexane (maintained at 60 °C) reacts with 1,4-diphenylbutadiyne (5 mol equiv) to yield the novel clusters **2** (60%) and **3** (30%). Both **2**[8] and **3**[9] have been fully characterized by

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(1) (a) Yanez, R.; Lugan, N.; Mathieu, R. *Organometallics* **1990**, *9*, 2998. (b) Knox, S. A. R.; Stansfield, R. F. D.; Stone, F. G. A.; Winter, M. J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1982**, 173.

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