drogenation, isomerization, and olefin dimerization mechanisms.[11-14]

Registry No. C_6D_6, 1076-43-3; $(i\text{-}Pr_3P)_2IrH_5$, 53470-70-5; neohexene, 558-37-2.

(11) Although metallacycles have been proposed, the interactions of ethylene with $(C_5H_4)(C_5H_5)_3Ti_2$ may involve vinyl activation (Pez, G. P. *J. Chem. Soc., Chem. Commun.* **1977**, 560–561. McDermott, J. X.; Wilson, M. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6529–36.). Although conventional olefin dimerization paths may well be operative, vinyl activation might be considered in some propene dimerizations [Baudry, D.; Cormier, J.-M.; Ephritikhine, M.; Felkin, H. *J. Organomet. Chem.* **1984**, *277*, 99–103. Green, M. L. H.; Knight, J. *J. Chem. Soc., Dalton Trans.* **1974**, 311–319.

(12) Stoichiometric vinyl activation has been observed with some clusters: (a) Deeming, A. J.; Hasso, S.; Underhill, M. *J. Organomet. Chem.* **1974**, *80*, C53. (b) Keister, J. B.; Shapley, J. R. *J. Organomet. Chem.* **1975**, *85*, C29. (c) Johnson, B. F. G.; Kelland, J. W.; Lewis, J.; Mann, A. L.; Raithby, P. R. *J. Organomet. Chem.* **1976**, *113*, C42; *J. Chem. Soc., Chem. Commun.* **1980**, 547.

(13) Metal–vinyl complexes have also been obtained with some bimetallic systems: Davies, D. L.; Dyke, A. F.; Endesfelder, A.; Knox, S. A. R.; Naish, P. J.; Orpen, A. G.; Plaas, D.; Tayler, G. E. *J. Organomet. Chem.* **1980**, *198*, C43. (b) Nubel, P. O.; Brown, T. L. *J. Am. Chem. Soc.* **1982**, *104*, 4955; **1984**, *106*, 644–652; **1984**, *106*, 3474–3484 (this system also shows modest oligomerization catalysis). (c) Franzeb, K.-H.; Kreiter, C. G. *J. Organomet. Chem.* **1983**, *246*, 189. (d) King, J. A., Jr.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1983**, *105*, 4846–8.

(14) Olefins containing donor atoms also undergo vinyl activation: (a) Kliegman, J. M.; Cope, A. C. *J. Organomet. Chem.* **1969**, *16*, 309. (b) Van Baar, J. F.; Vrieze, K.; Stufkens, D. J. *J. Organomet. Chem.* **1975**, *85*, 249. (c) Foot, R. J.; Heaton, B. J. *J. Chem. Soc., Chem. Commun.* **1973**, 838. (d) Komiya, S.; Ito, T.; Cowie, M.; Yamamoto, A.; Ibers, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 3874–3884. (e) Aumann, R.; Henkel, F.; Krebs, B. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 204.

Preparation of Reactive Low-Valent Bis(diphenylphosphino)methane-Bridged Mo–Ru Complexes. Facile Heterobimetallic Activation of Molecular Hydrogen

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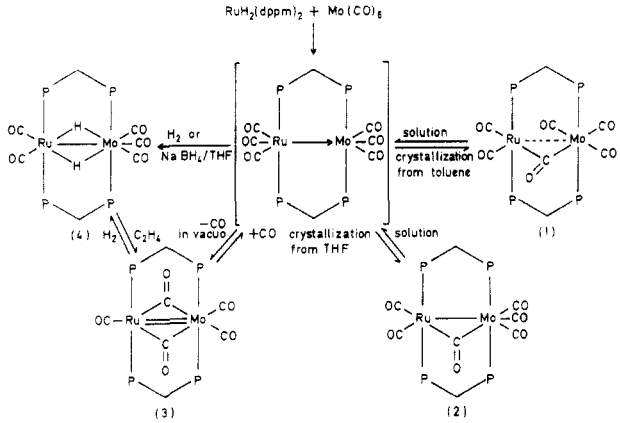
Summary: The reaction between $RuH_2(dppm)_2$ (dppm = bis(diphenylphosphino)methane) and $Mo(CO)_6$ at 80 °C produces $MoRu(CO)_6(dppm)_2$ which exists in three different interconvertible forms whether in solution, recrystallized from toluene (**1**) or tetrahydrofuran (**2**). $MoRu(CO)_6(dppm)_2$ loses CO reversibly at 80 °C in toluene in vacuo to give $MoRu(CO)_5(dppm)_2$ (**3**) which contains two bridging carbonyl groups. Dihydrogen adds to **3** at room temperature to give the dihydrido-bridged complex $MoRuH_2(CO)_5(dppm)_2$ (**4**). The crystal structure of **1** ($MoRu(CO)_6(dppm)_2 \cdot 5C_6H_5CH_3$) shows the complex to contain a long Mo–Ru distance and an "atypical" semibridging carbonyl group with a long C–O bond, in agreement with its low stretching frequency.

Heterobimetallic complexes are attracting considerable attention but as noted earlier, relatively few unsaturated complexes have been prepared and their reactivity studied.[1,2] These compounds are of particular interest when they are capable of easy reversible reactions with molecules like CO or H_2. Thus the production of heterobimetallic dihydrides, with each hydride possessing a distinct character, would be a key step in the reduction of polar molecules like CO.[3] Following our interest in heterobimetallic complexes,[4,5] we attempted the preparation of such molybdenum–ruthenium compounds. These compounds have not received much attention,[6,7] whereas Rh–Mo complexes, for example, are known.[3,8] We used $RuH_2(dppm)_2$[9] as starting material, as dppm seems a very good ligand for stabilizing heterobimetallic complexes.[10] We describe the preparation of $MoRu(\mu\text{-}CO)(CO)_5(dppm)_2$, a reactive complex which readily loses 1 mol of CO to give an unsaturated complex. Its reactivity in particular toward H_2 is of special interest.

Scheme I. Preparation and Reactivity of $MoRu(CO)_6(dppm)_2$: Proposed Structure for the Complexes



$RuH_2(dppm)_2$ reacts with 1 equiv of $Mo(CO)_6$ in toluene at 80 °C to give an orange solution from which orange crystals analyzing for $MoRu(CO)_6(dppm)_2$ (**1**) deposit after being cooled. Recrystallization from THF affords another compound (**2**) of the same formula as yellow crystals. Both compounds are shown by EDAX[11] to contain molybdenum and ruthenium. **1** and **2** have different infrared spectra in the 2100–1600 cm^{-1} region in the solid state. One striking difference is the presence of a band at 1685 cm^{-1} for **1** which shifts to 1715 cm^{-1} in the case of **2**. Nevertheless, both compounds when dissolved in CH_2Cl_2 or THF exhibit the same infrared spectrum which is different from the solid-state spectra. In that case no band below 1800 cm^{-1} is observed.[12] As expected the NMR spectra of **1** and

(1) (a) Roberts, D. A.; Geoffroy, G. L. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Eds.; Pergamon Press: Oxford, 1982; Chapter 40; (b) Breen, M. J.; Geoffroy, G. L.; Rheingold, A. L.; Fultz, W. G. *J. Am. Chem. Soc.* **1983**, 105, 1069.

(2) Breen, M. J.; Duttera, M. R.; Geoffroy, G. L.; Novotnak, G. C.; Roberts, D. A.; Shulman, M. P.; Steinmetz, G. R. *Organometallics* **1982**, *1*, 1009.

(3) Casey, C. P.; Bullock, R. M.; Nief, F. *J. Am. Chem. Soc.* **1983**, *105*, 7574.

(4) Sabo, S.; Chaudret, B.; Gervais, D. *J. Organomet. Chem.* **1983**, *258*, C19.

(5) Chaudret, B.; Delavaux, B.; Poilblanc, R. *Nouv. J. Chim.* **1983**, *7*, 679. Delavaux, B.; Chaudret, B.; Dahan, F.; Poilblanc, R. *Organometallics* **1985**, *4*, 935.

(6) Vollhart, K. P. C.; Weidman, T. W. *Organometallics* **1984**, *3*, 82.

(7) Sabo, S.; Chaudret, B.; Gervais, D. *J. Organomet. Chem.*, in press.

(8) (a) Carlton, L.; Lindsell, W. E.; McCullough, K. J.; Preston, P. N. *J. Chem. Soc., Chem. Commun.* **1982**, 1001; (b) *J. Chem. Soc., Dalton Trans.* **1984**, 1693.

(9) Chaudret, B.; Commenges, G.; Poilblanc, R. *J. Chem. Soc., Dalton Trans.* **1984**, 1635.

(10) See, for example: Blagg, A.; Hutton, A. T.; Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1984**, 1815 and references therein.

(11) EDAX: energy dispersive analysis by X-ray.

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2 in solution are the same. Thus the ^{31}P NMR spectrum shows an AA'BB' pattern characteristic for bis dppm-bridged heterobimetallic complexes which was simulated.[4,5,10] In the ^{1}H NMR spectrum only phenyl groups together with a pseudoquintet for the methylene protons are observed as for related complexes.[13] Finally, only one peak for the CO groups is observed by ^{13}C NMR spectrum, at room temperature, thus confirming the fluxionality of the molecule. These data led us to propose for **2** the classical structure (shown in Scheme I) containing two 18-electron moieties bound by a metal–metal bond as well as a "ketonic" bridging CO group. The more puzzling structure of **1** was elucidated by X-ray crystallography.[14]

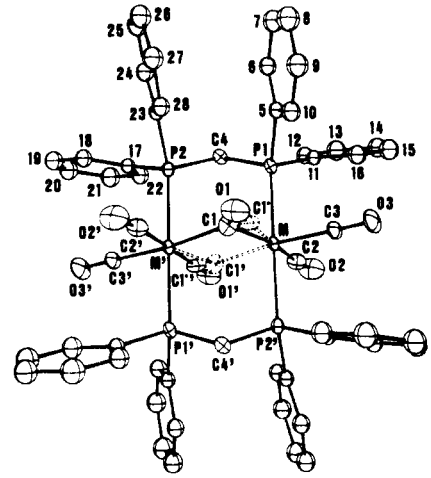

Figure 1. ORTEP view of $MoRu(CO)_6(dppm)_2$ (**1**). Thermal ellipsoids are drawn at the 30% probability level. The asterisk designates disordered C(1) atoms and the prime atoms related by centrosymmetry. Selected bond lengths (Å) and angles (deg) are as follows: M···M' = 3.058 (1), M–C(1) = 1.97 (4), M–C(2) = 1.96 (1), M–C(3) = 1.919 (9), M–C(1)* = 2.01 (4), M–C(1)' = 2.36 (3), C(1)–O(1) = 1.42 (4), C(1)*–O(1) = 1.07 (4); M–C(1)–O(1) = 130 (2), M'–C(1)–O(1) = 140 (2), M–C(1)–M' = 89 (1), M–C(1)*–O(1) = 180 (3).

The molecular structure is shown on Figure 1 as well as the atom numbering scheme and selected bond distances and angles. The structure shows a disorder not unusual in such complexes.[15] The bimetallic structure is bridged by two trans dppm groups: the molybdenum center accommodates three terminal carbonyl groups whereas two others are on the ruthenium. The sixth carbonyl group occupies the bridging position. The metal–metal distance (3.058 (1) Å) is quite long but does not rule out the presence of a metal–metal interaction. The mode of bonding of the bridging carbonyl group could be described as an "atypical" semibridge. In particular, the C–O bond distance is very long, in agreement with low stretching frequency. Of course the found values C(1)–O(1) = 1.42 (4) Å and C(1)*–O(1) = 1.07 (4) Å are outside normal ranges probably due to the presence of two close but different and thus unresolvable O(1) positions. Nevertheless it seems that a lengthening of the C(1)–O(1) distance is observed.

The structure in solution of $MoRu(CO)_6(dppm)_2$ is difficult to ascertain; one possibility of fitting the data is shown on Scheme I. In the absence of a bridging carbonyl group, one metal center would have 16 electrons (for steric reasons it must be molybdenum) whereas the other would contain 18 electrons. The presence of a donor–acceptor bond is thus possible. An alternative possibility could be the presence of a "normal" semibridging carbonyl group revealed by the medium-intensity band at 1800 cm^{-1}.

$MoRu(CO)_6(dppm)_2$ does not react with CO in solution, probably for steric reasons, but contains a labile carbonyl group since when heated at 80 °C in toluene in vacuo, it is transformed into a very air-sensitive red complex analyzing for $MoRu(CO)_5(dppm)_2$ (**3**). The infrared spectrum of **3**, whether in solution or in the solid state, shows five CO stretching bands, two of which are attributed to bridging carbonyl groups.[17] The spectroscopic data are

(12) Spectroscopic data for $MoRu(CO)_6(dppm)_2$: IR (CH_2Cl_2) 2000 (m), 1950 (s), 1925 (s), 1845 (s), 1800 (m) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 3.55 (quint, PCH_2P, J_{P-H} = 4 Hz); ^{31}P NMR (C_6D_6) AA'BB' δ_A 44.1, δ_B 36.1; ^{13}C NMR (CD_2Cl_2) δ 43.5 (t, P–C–P, J_{P-C-P} = 15 Hz) δ 219.2 (br, CO). Anal. Calcd for $MoRuC_{56}H_{44}O_6P_4 \cdot C_7H_8$ (**1**): C, 61.71; H, 4.24; Mo, 7.84; P, 10.12. Found: C, 60.93; H, 4.63; Mo, 7.47; P, 9.49. **1**: IR (Nujol) 1955 (sh), 1943 (s), 1928 (s), 1875 (s), 1820 (s), 1685 (m) cm^{-1}. Anal. Calcd for $MoRuC_{56}H_{44}O_6P_4 \cdot C_4H_8O$ (**2**): C, 59.75; H, 4.31; Mo, 7.97; P, 10.29. Found: C, 59.06; H, 4.69; Mo, 7.80; P, 9.97. **2**: IR (Nujol) 1993 (s), 1948 (s), 1910 (s), 1872 (s), 1843 (s), 1717 (m) cm^{-1}.

(13) Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1983**, 889.

(14) The crystal had to be mounted in a glass capillary under argon in the presence of the supernatant toluene solution which explains the presence of five solvent molecules in the crystal and the difference from analytical data obtained on samples which have been pumped in vacuo.

Crystal data: $C_{91}H_{84}O_6P_4MoRu$; M_r = 1953, triclinic, a = 12.491 (2) Å, b = 15.964 (2) Å, c = 11.339 (2) Å, α = 101.69 (1)°, β = 111.92 (1)°, γ = 96.22 (1)°, V = 2011.5 Å^3 (by least-squares refinement on a CAD4 diffractometer for 25 automatically centered reflections, λ = 0.710 69 Å), space group $P\bar{1}$ (C_i^1, no. 2), Z = 1, D_{calcd} = 1.31 g·cm^{-3}; red, air-sensitive rhombic crystals sealed in a Lindemann capillary filled with a toluene solution, μ(Mo Kα) = 4.63 cm^{-1} (T = 293 K).

Data Collection and Processing (Mosset, A.; Bonnet, J.-J.; Galy, J. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1977**, *B33*, 2639–2644). Intensity data were recorded by the θ–2θ scan technique (scan width 0.90 + 0.35 tan θ). A first set of 3593 reflections was collected (scan speed 1.3–10.1 deg·min^{-1}), 2917 of which were kept, standard intensity reflections abruptly decreasing (more than 50%). Crystal was reduced in height, "corroded" by solvent. After reorientation, data collection was continued starting again from standards fall, at a new rate of 2.9–20.1 deg·min^{-1}. A total of 1645 reflections were thus recorded until new standard intensities decrease. The two data sets ($1.5 < \theta < 20°$, $\pm h, \pm k, l$) gave 4562 independent reflections corrected for Lorentz and polarization effects and for anisotropic crystal decay, ca. 15% (Frentz, B. "SDP", structure determination package; Enraf-Nonius: Delft, Holland, 1982), 2942 of which with $I > 4\sigma(I)$ being considered "observed" and used in structure solution and refinement. No absorption corrections were made.

Structure Determination. As there is one molecule in the asymmetric unit, noncentrosymmetric space group $P1$ was first assumed. Metal atoms were located from a Patterson map. Subsequent full-matrix least-squares refinement and interpretation of difference Fourier maps using SHELX (Sheldrick, G. M. "SHELX76", program for crystal structure determination; University of Cambridge: Cambridge, England, 1976) enabled the location of the $MoRu(CO)_6(dppm)$ molecule and that of five toluene molecules. The bridging carbon atom presents disorder, as does a toluene molecule. Severe correlation factors between least-squares refinement matrice elements and normal temperature factors argued that, in fact, the space group is centrosymmetric, i.e., $P\bar{1}$. It then was shown by energy dispersive analysis by X-ray that the crystal used for data collection contained both Mo and Ru atoms. Structure resolution was achieved in the $P\bar{1}$ space group. The metal atom (m) was given Tc scattering factors, intermediate of Mo and Ru ones. Neutral scattering factors were used, those for the non-hydrogen atoms being corrected for anomalous dispersion (f', f'') ("International Tables for X-ray Crystallography"; J. A., Ibers, W. C. Hamilton Eds.; Kynoch Press, Birmingham, England, 1974; Vol. IV, Table 2.2.B, pp 99–101; Table 2.3.1, p 149; Table 2.2.c, p 102). The disordered carbon atoms were assigned 0.5 occupancy factors. Metal, P, CO, and methylene atoms were refined anisotropically. All phenyl rings were refined as isotropic rigid groups (C–C = 1.385 Å). Hydrogen atoms were introduced in calculations in constrained geometry (C–H = 0.95 Å). For the "half" disordered toluene molecule around one origin, no methyl or hydrogens were found.

The final full-matrix least-squares refinement converged to R = 0.050 and R_w = 0.056 with unit weights. The error in an observation of unit weight was S = 2.26 with 2942 observations and 189 variables. In the last cycle of refinement the shifts were less than 0.06σ for all parameters but those of the disordered carbon atoms (<0.8σ). A final difference Fourier map showed no excursion of electron density greater than 0.5 e/Å^3.

(15) Delavaux, B.; Chaudret, B.; Taylor, N. J.; Arabi, S.; Poilblanc, R. *J. Chem. Soc., Chem. Commun.* **1985**, 805.

(16) For the different modes of bonding of bridging carbonyl groups, see, for example: Colton, R.; McCormick, M. J. *Coord. Chem. Rev.* **1980**, *31*, 1.

in agreement with the proposed structure shown on Scheme I. It is noteworthy that the low-temperature ^{13}C NMR spectrum shows three CO peaks, one of which is attributable to the bridging CO, and that the ^{31}P NMR spectrum is solvent and temperature dependent.[17] Thus in CD_2Cl_2 an AA'BB'-type spectrum is observed at room temperature, whereas in C_7D_8 a singlet is observed at room temperature which splits into a badly resolved AA'BB' pattern at 200 K. This was attributed to small variations of the chemical shift of the phosphorus AA' and BB' as a function of solvent polarity and temperature. The proposed formula implies the presence of two 16-electron metal centers close to one another. It is thus reasonable for this species to propose the existence of a double metal–metal bond as for related complexes.[8]

1, **2**, and **3** all react rapidly in a THF or toluene solution with dihydrogen (room temperature and pressure) to give a yellow complex analyzing for $MoRuH_2(CO)_5(dppm)_2$ (**4**). Spectroscopic data[18] (infrared and ^{13}C NMR spectroscopy) are in agreement with the presence of five terminal CO groups according to a local C_{2v} symmetry. The ^{31}P NMR spectrum in C_7D_8 shows again a single peak split into an AA'BB'-type spectrum at 200 K. Finally, the ^1H NMR spectra recorded at variable temperature are in agreement with the presence of two equivalent bridging hydrides in the complex (see Scheme I). The hydride signal is a multiplet at room temperature becoming a pseudotriplet at 263 K ($J_{P-H\ apparent}$ = 15 Hz) and finally a single broad peak at 203 K. It has not been possible to gain information on the real coupling constants partly because of the close proximity of the AA' and BB' signals in ^{31}P NMR preventing a selective phosphorus decoupling. This reaction represents a rare case of heterobimetallic activation of molecular hydrogen. The mechanism probably involves the presence of a 16-electron ruthenium intermediate capable of activating H_2 followed by rearrangement of the complex. It is noteworthy that this reaction can be reversed by passing ethylene through a solution of **4**; **3** is rapidly obtained.

Attempts to reduce $MoRu(CO)_6(dppm)_2$ with $NaBH_4$ or $KBH(sec\text{-}Bu)_3$ in THF only led to the dihydride **4**. The mechanism of this reaction remains obscure.

Finally, $MoRu(CO)_6(dppm)_2$ can easily be electrochemically oxidized through two one-electron processes, respectively, at 303 and 706 mV. The first oxidation is quasi-reversible (I_{PF}:I_{PB} = 0.78).

We are presently studying the high reactivity of this system.

Acknowledgment. We thank Dr. J. Devillers for help in the resolution of NMR spectra.

Supplementary Material Available: Tables of structure factor amplitudes, final atomic coordinates, final anisotropic thermal parameters, hydrogen atomic positional and thermal parameters, and bond lengths and angles for $[MoRu(CO)_6(dppm)_2 \cdot 5(PhMe)$ (19 pages). Ordering information is given on any current masthead page.

(17) Anal. Calcd for $MoRuC_{55}H_{44}O_5P_4$ (**3**): C, 59.73; H, 3.98; Mo, 8.69; P, 11.22. Found: C, 59.36; H, 4.33; Mo, 8.28; P, 10.92. **3**: IR (Nujol mull or CH_2Cl_2) 1967 (s), 1900 (vs), 1875 (s), 1787 (s), and 1722 (m) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 3.1 (q, PCH_2P, J_{P-H} = 4 Hz); ^{31}P NMR ($C_6D_5CD_3$) 299 K, δ 35.9, 200 K, AA'BB' δ_A 33, δ_B 31, (CD_2Cl_2) AA'BB' δ_A 45.3, δ_B 37.9; ^{13}C NMR (CD_2Cl_2) 203 K, δ 43.1 (br, P–C–P), 215.7, 217.6, 238.6 (br, CO).

(18) Anal. Calcd for $MoRuC_{55}H_{46}O_5P_4$ (C_5H_{12}) (**4**): C, 61.07; H, 4.92; Mo, 8.14, P, 10.52. Found: C, 60.16; H, 4.69; Mo, 7.52; P, 10.24. **4**: IR (Nujol mull or CH_2Cl_2) 2015 (s), 1960 (s), 1900 (s), 1860 (vs), 1805 (s) cm^{-1}; ^1H NMR ($C_6D_5CD_3$) δ 3.95 (br, PCH_2P), −7.95 (m, hydrides); integration ratio of CH_2:hydrides = 4:2; ^{31}P NMR ($C_6D_5CD_3$) 300 K, δ 41.2, 200 K, AA'BB' δ_A 41.5, δ_B 38.5; ^{13}C NMR ($C_6D_5CD_3$, 193 K) δ 40.2 (br, P–C–P), 202.9, 216.2, 226.0 (all br, CO).