results in a large splitting of the metal "t_{2g}" set (descending from O_h symmetry) such that this orbital is 2.23 eV above the other two. Compound 1′ is unusual in that it is a formally d^4, 16-electron complex and its stability is attributed to the strong splitting of the metal orbitals which concomitantly results in a substantial separation between the HOMO and LUMO. It is the strong π-acidity of the NO ligand in conjunction with a ligand set that by necessity generates a nonbonding d orbital which causes this splitting and allows such a complex to exist. Consistent with this, the carbonyl analogue (CO is generally considered to be a weaker π-acceptor ligand than NO^+ [9-11]) $CpM(CO)R_2$ (M = Mn, Tc, or Re) is not known and would not be expected to be stable.

If we compare the molecular orbital picture of 2′ (right half of Figure 1) to that of 1′, the opposite picture emerges. The oxo ligand is a very good π-donor (as well as a good σ-donor) and interacts with the Re 5d orbitals to strongly destabilize two levels. This leads to a formal metal–oxo triple bond consisting of one σ- and two π-contributions.[12] As in 1′, the methyl ligands are σ-only donors, and, once again, the geometry dictates that one d orbital (5a′) remains nonbonding. Compound 2′ contains Re in the +5 oxidation state (d^2); therefore, the nonbonding 5a′ becomes the HOMO. As before, it is the large splitting of the pseudo-t_{2g} set which allows for a substantial separation (2.36 eV, comparable to that in 1′) to exist between filled and unfilled levels. However in 1′ the splitting was the result of strong π-accepting from nitrosyl to stabilize two orbitals below one, whereas in 2′ the converse effect is observed as strong π-donation from the oxo ligand destabilizes two orbitals above one.

As was mentioned earlier, most low-valent organometallic complexes adhere to the 18-electron rule, a rule that is especially relevant when all three of the pseudo-t_{2g} orbitals are stabilized as in $CpM(CO)_3$ (M = Mn, Re).[13] The fact that the 16-electron 1 is an exception to this rule was explained by the electronic properties of its nitrosyl ligand and by the geometric generation of a nonbonding d orbital. The 18-electron analogue of 1 would be expected to be stable since the additional two electrons would reside in the nonbonding 5a′ orbital and a substantial HOMO–LUMO gap would still be present. Consistent with this analysis, $CpRu(NO)(CH_2SiMe_3)_2$ has been prepared.[14] In the case of high-valent organometallic complexes the 18-electron rule is no longer valid as the d levels are generally destabilized by π-donors and would rather remain unoccupied. Indeed, all known piano-stool systems containing at least two oxo ligands (thereby guaranteeing that all three pseudo-t_{2g} orbitals are destabilized) are d^0 as is the case for $CpW(O)_2R$,[3b] $CpMo(O)_2X$,[3c] or Cp^*ReO_3.[3d] The nonbonding orbital generated in 2′ allows for the violation of this "d^0 rule".[15] Further, just as the 18-electron analogue of 1′ can be generated by occupying its nonbonding orbital, it is to be expected that the d^0 analogue of 2′ (which results from the *removal* of electrons from its nonbonding orbital) should exist. Such a compound, namely, $CpV(O)Ph_2$,[3a] is known. In fact, for the series $CpM(O)Cl_2$ (which is homologous to the oxo–alkyl complexes discussed above), d^0 (M = V,[3e] d^1 (M = Mo),[3c] and d^2 (M = Re)[3f] examples are known, underscoring the facility with which the nonbonding orbital can be occupied and deoccupied.

We believe that molecular orbital theory can prove to be very useful in understanding the connections between the relatively mature area of low-valent organometallic chemistry and the relatively unexplored area of high-valent organo transition-metal chemistry. To this end, subsequent contributions will address such connections in both mono- and dinuclear piano-stool systems.

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Reaction of $(\mu\text{-}C_7H_7)Ru(CO)_3Rh(CO)_2$ with Bis(diphenylphosphino)methane: Conclusive Demonstration of the Importance of Cycloheptatrienyl Ring Slippage in CO Substitution Reactions

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Summary: The reaction of $(\mu\text{-}C_7H_7)Ru(CO)_3Rh(CO)_2$ with bis(diphenylphosphino)methane (DPPM) gives $(\mu\text{-}C_7H_7)(\mu\text{-}DPPM)Ru(CO)_2Rh(CO)$. The progress of the reaction was followed by low-temperature ^{31}P NMR spectroscopy. This allowed the identification of two well-defined intermediates prior to final product formation and conclusively established that CO substitution proceeds via hapticity changes of the bridging cycloheptatrienyl moiety.

According to currently held wisdom, ring slippage accompanied by η^5 to η^3 bonding mode changes is responsible for both the associative nature of the substitution process in cyclopentadienyl[1] and indenyl[2] metal carbonyls and for the greatly enhanced reactivity of the latter type compounds over their cyclopentadienyl analogues (the "indenyl effect"[3]). Recently ligand-induced η^5 to η^3 conversion was conclusively demonstrated by the isolation and structural characterization of (η^3-indenyl)IrL_3 (L = $P(CH_3)_3$, $P(CH_3)_2(C_6H_5)$) from (η^5-indenyl)Ir(η^2-cyclooctene)$_2$.[4]

During our studies on the $^{13}CO/CO$ exchange and phosphine substitutional processes in $(\mu\text{-}C_7H_7)Fe(CO)_3Rh(CO)_2$ we were led to postulate similar hapticity changes of the bridging C_7H_7 ring in order to account for the facility of these reactions.[5] Here we wish to report direct and unambiguous NMR evidence that substantiates this proposal.

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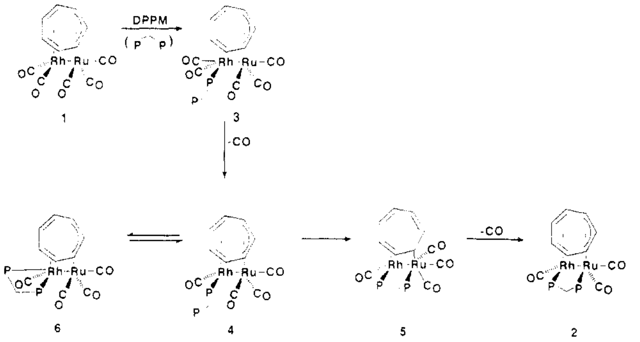
Scheme I. Mechanism for the Formation of $(\mu\text{-}C_7H_7)(\mu\text{-}DPPM)\overline{Ru(CO)_2Rh}(CO)$ from $(\mu\text{-}C_7H_7)\overline{Ru(CO)_3Rh}(CO)_2$ and DPPM



The reaction of $(\mu\text{-}C_7H_7)\overline{Ru(CO)_3Rh}(CO)_2$ (1)[6] with 1 equiv of bis(diphenylphosphino)methane (DPPM) in hexane resulted in the precipitation of the DPPM-substituted compound 2 in good yield (eq 1).[7] Spectroscopic

$$1 + \text{DPPM} \xrightarrow[\text{room temp}]{\text{hexane}} \underset{2}{(\mu\text{-}C_7H_7)(\mu\text{-}DPPM)\overline{Ru(CO)_2Rh}(CO)} + 2CO \quad (1)$$

data on 2 clearly show the presence of bridging cycloheptatrienyl and DPPM units and terminal carbonyl groups. Since the analogous reaction with $(\mu\text{-}C_7H_7)\overline{Fe(CO)_3Rh}(CO)_2$ produced the Rh-chelated DPPM complex as the kinetic product,[5b] it was deemed essential to follow the reaction of 1 with DPPM by ^{31}P NMR spectroscopy in order to identify potential intermediate(s) and thereby elucidate the mechanism of formation of 2.

The ^{31}P NMR spectra, recorded at different temperatures and reaction times, are shown in Figure 1. It is clear from the figure that formation of 2 proceeds via well-defined intermediate steps. Scheme I details the proposed mechanism. The first species observed exhibits two ^{31}P NMR signals at δ 44.4 (dd) due to a rhodium-bound phosphorus donor and at δ −25.7 (d) in the region of uncoordinated DPPM ligand. There is no doubt that this intermediate contains an η^1-DPPM ligand but on the basis of ^{31}P NMR data alone a decision between 3 and 4 is not possible. However, preliminary ^{13}C NMR work supports its formulation as 4.[8] No such ambiguity exists concerning the nature of the next intermediate, which must be another DPPM-bridged Ru–Rh species, similar, yet different from the final product 2 (spectrum, T = −40 °C, t = 30 min; δ(P_{Rh}) 33.6 (dd), δ(P_{Ru}) 44.2 (d)). Inescapably, the unsaturation needed at the ruthenium center must be provided by the bridging cycloheptatrienyl ligand. Intramolecular attack by the free phosphorus atom of the dangling η^1-DPPM ligand on ruthenium thus proceeds by displacement of a double bond of the $\mu\text{-}C_7H_7$ moiety, without CO loss, to give 5. The latter at −40 °C slowly and more rapidly at higher temperatures loses CO to give 2. It is interesting to note that the exchange of environment of the two ends of the η^1-DPPM moiety in 4, as seen by line broadening at −20 °C, provides evidence for dissociation of a cycloheptatrienyl double bond at the Rh center as well, equilibrium between 4 and 6 in Scheme I. These findings represent the first conclusive demonstration of the flexible bonding capability of the $\mu\text{-}C_7H_7$ moiety and establish unequivocally the ability of the ligand to provide "incipient coordinative unsaturation" at metal centers.

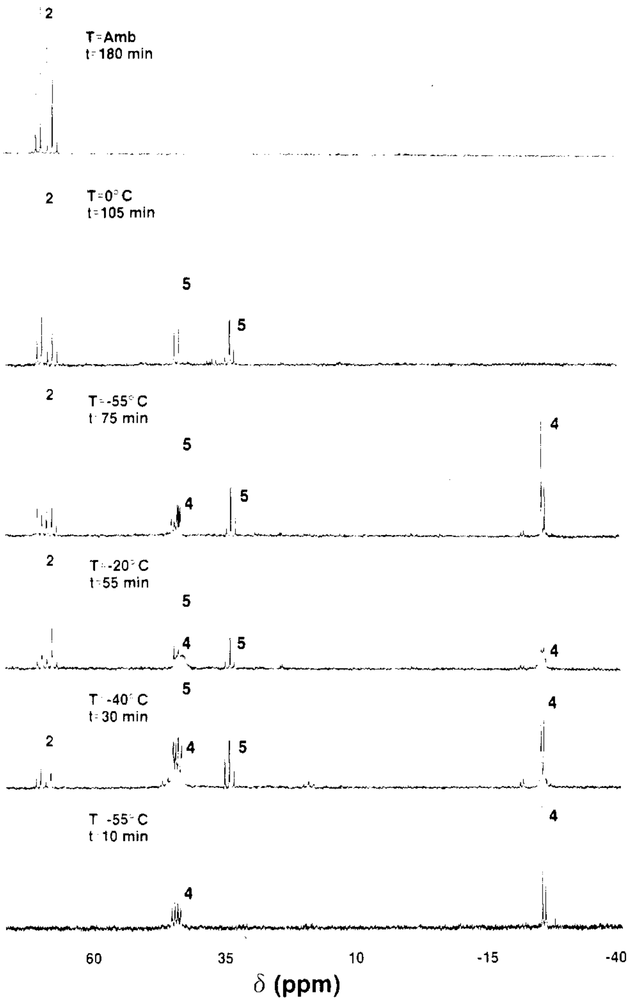


Figure 1. $^{31}P\{^1H\}$ NMR study of the reaction of $(\mu\text{-}C_7H_7)Ru(CO)_3Rh(CO)_2$ with DPPM.

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Registry No. 1, 109584-63-6; 2, 109584-64-7; 4, 109584-65-8; 5, 109584-66-9; DPPM, 2071-20-7.

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(7) 2: red solid; IR (CH_2Cl_2) ν_{CO} 1975 (s), 1940 (s), 1904 (br) cm^{-1}; ^1H NMR (CD_2Cl_2, −80 °C) δ 3.90 (s, C_7H_7), 4.05 (q, CH_2, 1 H), 1.95 (q, CH_2, 1 H), 7.2–7.4 (m, C_6H_5); ^{13}C NMR (CD_2Cl_2, −75 °C) δ 61.0 (s, C_7H_7), 125–128 (C_6H_5), 201.7 (dd, CO_{Rh}, J_{Rh-C} = 77.7 Hz, J_{P-C} = 12.4 Hz), 209.6 (s) and 199.7 (d, J_{P-C} = 7.0 Hz) CO_{Ru}; ^{31}P NMR (CD_2Cl_2, 25 °C) AB of ABX pattern, P_{Ru} δ 70.58 (J_{P-P} = 139.4 Hz, J_{Rh-P} = 2.3 Hz), P_{Rh} δ 68.41 (J_{P-P} = 139.4 Hz, J_{Rh-P} = 154.5 Hz); MS (70 eV, 125 °C) $M^+ - n$CO (n = 1–3); yield 85%. Anal. $C_{35}H_{29}RuO_3P_2Rh$: C, H.

(8) A ^{13}C NMR spectrum of a solution containing only the first species appearing in Figure 1 (CD_2Cl_2, T = −55 °C, t = 10 min) showed two resonances in the carbonyl region in a 3:1 intensity ratio at δ 218.3 (br s, due to the three averaged RuCO groups) and at δ 203.1 (dd, J_{Rh-C} = 90.5 Hz, J_{P-C} = 11.8 Hz, due to the single RhCO group). Spectra recorded at higher temperatures and longer reaction times were too complicated to allow unambiguous assignment to other species.