regioselectivity of the deuteride addition. The reaction rate for this addition is fast. Therefore, in order to keep a high ratio of relative rates of different pathways, it appears that a low reaction temperature is advisable. The regioselectivity for the addition is >98% cis to the nitrosyl with use of this procedure.

The yields of the nucleophilic addition products are high. For practical use in organic synthesis, high yield methods for removing the resulting olefin from the metal are required. Oxidation by ceric ion is fast and effective but can sometimes lead to contamination with fragments from the neomenthyl group or oxidation of the product. We have chosen air oxidation because it is mild (albeit slow) and quantitative. Generally, removing the olefin from the metal is not a problem; but, separating the olefin from the solvent and organic decomposition products may be difficult. In practical applications, the intended use of the product might well determine the method of choice.

We have discussed some of the origins of the selectivity previously,[4,18,20] and the subject is still under investigation. The electronic asymmetry of the metal environment plays an important role. Some of the effects of the electronic asymmetry can be seen in Figure 1 and Table III. In particular one might note that the C(1)–C(3) carbons of the allyl tend to align parallel to the Mo–Br bond. This can be attributed to relative depletion of the back-bonding in the d-orbital parallel to the Mo–N–O bond relative to that parallel to the Mo–Br bond.[20] Also the Mo–C(1) bond length is considerably shorter than the Mo–C(3) length [i.e., 2.373 (6) and 2.544 (7) Å]. The ring appears to constrain the C(1)–C(2) and C(2)–C(3) lengths to comparable distances [1.403 (9) and 1.364 (9) Å] whereas the difference is significant in open-chain allyls.[21-23]

The carbonyl nitrosyl cations show a similar tendency for the allyl group to orient parallel to the Mo–C–O bond. The most important consequence of the electronic asymmetry, however, is its ability to effect reaction at the position cis to the NO in the exo isomer. This has provided an effective synthetic procedure for the preparation of chiral allylically substituted olefins in high optical purity. It appears that this approach may be particularly useful for mechanistic studies[24] when one needs a preparation of optically active hydrocarbons in which the chirality arises solely from the isotopic differences between H and D atoms.

Acknowledgment. We wish to thank the National Science Foundation for support of the NSF Northeast Regional NMR Facility (Grant CHE79-16210). The work was supported by the NSF (Grant CHE82-08042).

Registry No. NMCpMo$(CO)_2(\eta^3\text{-}C_8H_{13})$, 89689-87-2; $[(CH_3CN)_2MoBr(CO)_2(\eta^3\text{-}C_8H_{13})]$, 81923-03-7; (+)-[NMCpMo(NO)(CO)$(\eta^3\text{-}C_8H_{13})]BF_4$, 89689-90-7; (+)-[NMCpMo(NO)(CO)$(\eta^3\text{-}C_8H_{13})]PF_6$, 89772-14-5; (–)-[NMCpMo(NO)(CO)$(\eta^3\text{-}C_8H_{13})]BF_4$, 89771-47-1; (+)-NMCpMo(NO)(Br)$(\eta^3\text{-}C_8H^{13})$, 89689-91-8; (–)-NMCpMo(NO)(Br)$(\eta^3\text{-}C_8H^{13})$, 89771-48-2; $(-)_D$-NMCpMo(NO)(CO)$(\eta^2\text{-}C_8H^{13}OH)$, 89689-92-9; $(-)_D$-NMCpMo(NO)(CO)$(\eta^2\text{-}C_8H^{13}D)$, 89689-93-0; $Mo(CO)_6$, 13939-06-5; $NOBF_4$, 14635-75-7; NaBr, 7647-15-6; 3-bromocyclooctene, 7422-06-2; (–)-cycloocten-3-ol, 62210-83-7; (–)-3-deuteriocyclooctene, 89689-94-1; silver hexafluorophosphate, 26042-63-7; neomenthylcyclopentadiene, 89689-88-3.

Supplementary Material Available: Tables of anisotropic temperature factors, calculated hydrogen atom positions, and structure factors for both crystal modifications of the bromide structure and tables of crystal data, positional parameters, bond lengths, and bond angles for the $P2_1$ modification (26 pages). Ordering information is given on any current masthead page.

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(23) The $P2_1$ crystal modification of this compound shows similar effects. The Mo–C(1) and Mo–C(3) lengths are 2.353 (7) and 2.547 (8) Å whereas the C(1)–C(2) and C(2)–C(3) lengths are 1.34 (1) and 1.34 (1) Å.

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Communications

Aryl Group Interchange between Triarylphosphines Catalyzed by Group 8 Transition Metals

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Summary: Group 8 transition metals catalyze intermolecular aryl scrambling of triarylphosphines. Reaction rates vary among metals and among different complexes of a metal.

Soluble transition-metal phosphine complexes are catalysts for a variety of industrial processes,[1] since they offer unique chemical properties and process advantages. Catalyst stability is an important consideration in these processes both because of the cost of the catalysts and because of the effects of changing catalyst activity on the process operation and efficiency.

Metal-catalyzed phosphine decompositions have been observed in several instances. For example, it has been known[2,5] that triphenylphosphine slowly decomposes during rhodium-catalyzed propylene hydroformylation to propyldiphenylphosphine. The direct carbon–phosphorus bond cleavage of triphenylphosphine has been observed with certain rhodium clusters,[3] as well as with mononuclear rhodium–phosphine complexes.[4]

Such phosphine decompositions both generate bypro-

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(2) Gregorio, G.; Montrasi, G.; Tampieri, M.; Cavalieri d'Oro, P.; Pagani, G.; Andreetta, A. *Chim. Ind. (Milan)* **1980**, *62*, 389.

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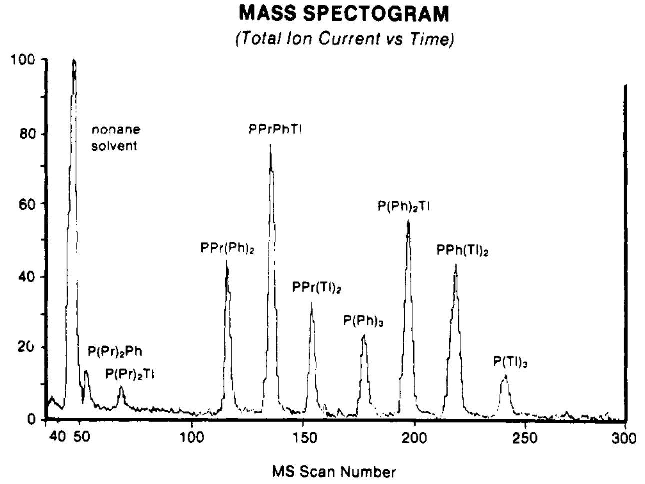

Figure 1. Gas chromatography–mass spectrometry of the products from the reaction of triphenylphosphine and tri-*p*-tolylphosphine in the presence of rhodium under an atmosphere of hydrogen and propylene: Ph = C_6H_5; Tl = *p*-$CH_3C_6H_4$; Pr = C_3H_7.

Table I. Rates of Aryl Group Interchange between Triphenylphenylphosphine and Tri-*p*-tolylphosphine Catalyzed by Rhodium Complexes[a]

catalyst precursor	reactn rate, μmol/min
$Rh(acac)(CO)(Ph_3P)$	56.8×10^{-3}
$RhCl(Ph_3P)_3$	17.6×10^{-3}
$RhCl(CO)(Ph_3P)_2$	2.3×10^{-3}
$Rh_4(\mu\text{-}CO)_2(\mu\text{-}Ph_2P)_4(CO)_3(Ph_3P)$	*b*
$Rh_6(CO)_{16}$	*b*

[a] Reaction conditions: temperature = 120 °C; 1000 ppm of rhodium; 100 psi of H_2; phosphine:rhodium mole ratio = 20. [b] Rate too low to measure, but some exchange was unambiguously observed.

ducts that may adversely alter the properties of the catalysts and offer pathways for catalyst deactivation.

During our studies of the rhodium-catalyzed triphenylphosphine reaction to form propyldiphenylphosphine that occurs during propylene hydroformylation[5] we observed a facile interchange of aryl groups between different triarylphosphines and between alkyldiarylphosphines (eq 1).

$$(C_6H_5)_3P + (p\text{-}CH_3C_6H_4)_3P \xrightarrow[C_3H_6,\ H_2,\ 130\ ^\circ C]{Rh} (C_6H_5)_2(p\text{-}CH_3C_6H_4)P + (C_6H_5)(p\text{-}CH_3C_6H_4)_2P + (C_6H_5)(CH_3C_6H_4)PC_3H_5 + (C_6H_5)_2PC_3H_7 + (p\text{-}CH_3C_6H_5)_2PC_3H_7 \quad (1)$$

The reaction products shown in eq 1 have been characterized by gas chromatography–chemical ionization mass spectroscopy. The mass spectrogram (total ion current vs. time) for this reaction mixture (Figure 1) shows that virtually complete equilibration between reactants and products has been achieved. Since the mole equivalents of phosphines employed are 20 times more than the mole equivalents of the rhodium catalyst, the aryl interchange reaction is clearly catalytic, and it is not the result of formation of intermediate rhodium complexes that stoichiometrically decompose with scrambling of aryl groups. With the complex $RhH(CO)(Ph_3P)_3$ as catalyst, aryl group scrambling between triphenylphosphine and tri-*p*-tolyl phosphine occurs under an atmosphere of propylene, or hydrogen, or nitrogen.[6]

Scheme I

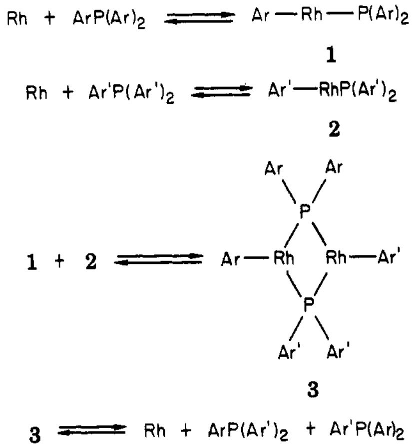

Table II. Rates of Aryl Group Interchange between Triphenylphosphine and Tri-*p*-tolylphosphine Catalyzed by Group 8 Transition Metals[a]

catalyst precursor	temp, °C	reactn rate, μmol/min
$Co_2(CO)_8$	130	490.5×10^{-3}
$Os_3(CO)_{12}$	130	36.1×10^{-3}
$Ni(CO)_2(Ph_3P)_2$	170	12.5×10^{-3}
$Pd(Ph_3P)_4$	170	7.5×10^{-3}
$Ru_3(CO)_{12}$	170	146.6×10^{-3}
$Rh_6(CO)_{16}$	170	19.2×10^{-3}

[a] Reaction conditions: phosphine:metal mole ratio = 20; 1000 ppm of metal catalyst; 100 psi of H_2:C_3H_6 (1:1).

The rates of aryl scrambling vary with the reaction atmosphere. Under propylene, chemical equilibrium is reached in 1 h, under nitrogen, in 3 h, and under hydrogen/propylene, in 4 h. When hydrogen alone is used, the reaction slows considerably after 3 h and complete equilibration is not achieved even after 18 h at 130 °C. Scrambling continues, however, upon heating at 170 °C. In every instance the solution turns dark brown, which is indicative of rhodium clustering.[7] We believe that the activity of rhodium is diminished as a result of clustering. This hypothesis is supported by the following results.

The rates of aryl group interchange between triphenylphosphine and tri-*p*-tolylphosphine were measured by using rhodium complexes (Table I) which reflect a variety of structures and catalytic reactivities. Highest rates are observed with mononuclear complexes such as $Rh(acac)(CO)Ph_3P$ and $RhCl(Ph_3P)_3$. Much lower rates

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(5) Abatjoglou, A. G.; Bryant, D. R. *Organometallics*, first paper of two in this issue.

(6) The aryl interchange reactions were performed in a 100-mL steel autoclave equipped with magnetic stirring and temperature and pressure controls. In a typical experiment a catalyst solution consisting of 0.0305 g (0.1184 mmol) of $Rh(acac)(CO)_2$, 0.338 g (1.11 mmol) of $(p\text{-}CH_3C_6H_4)_3P$, 0.291 g (1.11 mmol) of $(C_6H_5)_3P$, and 24.35 g of degassed nonane (toluene or benzene was used in some cases also) was syringed into the 120 °C preheated and nitrogen-purged reactor through a valve/septum assembly. After temperature equilibration about 100 psi of H_2 or H_2/C_3H_6 was added and samples were withdrawn every 5 min for 1 h. The concentration of the reaction products was determined by high-pressure liquid chromatography using an internal standard method. Conditions: column, 4.6 mm × 25 cm Zorbax ODS; solvent, acetonitrile–water (4:1); detector, UV at 254 mm; flow rate, 1.5 mL/min. All phosphines were determined as their phosphine oxides after oxidation with $t\text{-}BuO_2H$. $(p\text{-}FC_6H_4)_3PO$ was used as internal standard. Gas chromatography was avoided because some aryl interchange occurs in the injection port of the gas chromatograph. The reaction rates were determined from the slopes of the concentration vs. time plots. Where rates were very low, the determination was based on the concentration of product in the final sample. Positive identification of the scrambled phosphine products was obtained by gas chromatography–chemical ionization mass spectroscopy using an AEI Model MS-50 mass spectrometer interfaced with a Carlo-Erba gas chromatograph. Chromatographic conditions: column, 10 ft × $^1/_4$ in. OV-101; column temperature programmed 100–200 °C at 5 °C/min.

(7) Jamerson, J. D.; Pruett, R. L.; Billig, E.; Fiato, F. A. *J. Organomet. Chem.* **1980**, *193*, C43–C45.

are found with the more coordinatively and structurally stable clusters $Rh_6(CO)_{16}$ and $Rh_4(\mu\text{-}CO)_2(\mu\text{-}Ph_2P)_4(CO)_3(Ph_3P)$.[7] The stable mononuclear square-planar complex $RhCl(CO)(Ph_3P)_2$ also shows low activity. The low activity of the rhodium clusters is surprising if one assumes that aryl group interchange occurs between vicinal metal centers as is proposed by Kaneda et al.[3] It is possible that the rhodium clusters used in this study do not promote phosphine breakdown reactions at lower temperatures, because they are more coordinatively and structurally stable species. At the higher temperatures the breakdown of these clusters to more reactive mononuclear species and/or coordinatively unsaturated clusters is facilitated.

One possible mechanism (Scheme I) assumes that with the more reactive mononuclear rhodium complexes, the initial products of oxidative addition of the phosphine aryl–phosphorus bonds to rhodium species **1** and **2** can form phosphido-bridged intermediates **3**, which can exchange their aryl- and/or phosphido-bridging groups and thereby allow scrambling.

Catalysis of this reaction is not unique to rhodium. Other group 8 transition metals show varying degrees of activity (Table II). Of the metals screened, cobalt is the most active, but with it an induction period is observed. This may be due to the time required for the formation of the active catalyst from the catalyst precursor which is the insoluble reaction product of $Co_2(CO)_8$ with phosphines. Indeed when the catalyst solution starts becoming homogeneous, the scrambling reaction begins. The activities of the ruthenium cluster $Ru_3(CO)_{12}$ and the rhodium cluster $Rh_6(CO)_{16}$ are both very low at 130 °C, but at 170 °C the ruthenium cluster is significantly more active than the rhodium cluster.

Registry No. $Rh(acac)(CO)(Ph_3P)$, 25470-96-6; $RhCl(Ph_3P)_3$, 14694-95-2; $RhCl(CO)(Ph_3P)_2$, 13938-94-8; $Rh_4(\mu\text{-}CO)_2(\mu\text{-}Ph_2P)_4(CO)_3(Ph_3P)$, 75503-69-4; $Rh_6(CO)_{16}$, 28407-51-4; $Co_2(CO)_8$, 10210-68-1; $Os_3(CO)_{12}$, 15696-40-9; $Ni(CO)_2(Ph_3P)_2$, 13007-90-4; $Pd(Ph_3P)_4$, 14221-01-3; $Ru_3(CO)_{12}$, 15243-33-1; $Rh(acac)(CO)_2$, 14874-82-9; $(C_6H_5)_3P$, 603-35-0; $(p\text{-}CH_3C_6H_4)_3P$, 1038-95-5.

Reactivity of Some Alkyls and Aryls of Rhodium and Iridium toward Carbon Dioxide. Facile Formation and X-ray Structural Characterization of the Peroxocarbonato Complex *mer*-$\overline{\mathrm{Rh(4\text{-}MeC_6H_4)[OOC(O)O}}]$[$PhP(CH_2CH_2CH_2PPh_2)_2$][1]

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Summary: The reactivity of several organoiridium and -rhodium compounds $M(R)(CO)(PPh_3)_2$ and $M(R)[PhP(CH_2CH_2CH_2PPh_2)_2]$ toward carbon dioxide has been investigated. The title complex was obtained by pressuring THF solutions of $Rh(4\text{-}MeC_6H_4)[PhP(CH_2CH_2CH_2PPh_2)_2]$ to 30–60 bar with reagent grade carbon dioxide probably containing trace amounts of dioxygen. It could also be prepared by allowing the rhodium(I) precursor to react with deoxygenated CO_2 and a known amount of O_2. The structure of the peroxocarbonato derivative was determined by X-ray diffraction.

The current interest in transition metal–carbon dioxide chemistry[2] prompted us to screen some of our organoiridium and -rhodium compounds $M(R)(CO)(PPh_3)_2$[3] and $M(R)[PhP(CH_2CH_2CH_2PPh_2)_2]$[4] for their ability to bind CO_2. The preliminary results of this study are summarized in Table I.

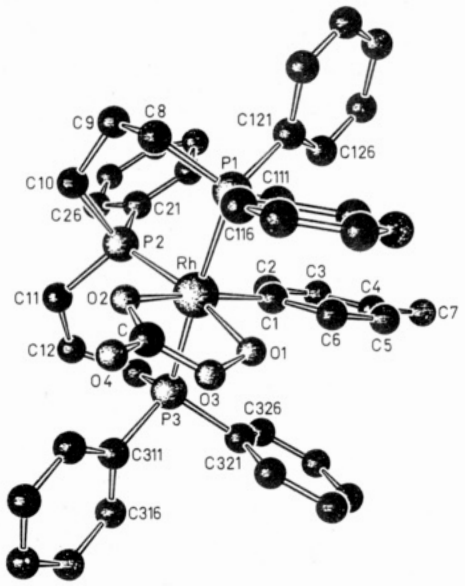

Figure 1. SCHAKAL drawing[7] of $\overline{\mathrm{Rh(4\text{-}MeC_6H_4)[OOC(O)O}}]$-(bdpp) (1). Selected bond lengths (Å): Rh–P1 = 2.269 (4), Rh–P2 = 2.289 (3), Rh–P3 = 2.348 (4), Rh–O1 = 2.034 (8), Rh–O2 = 2.127 (10), Rh–C1 = 2.056 (14), O1–O3 = 1.434 (15), O2–C = 1.273 (17), O3–C = 1.320 (21), and O4–C = 1.218 (20). $\overline{\mathrm{RhOOC(O)O}}$ bond angles (deg): O1–Rh–O2 = 77.3 (4), Rh–O2–C = 112.6 (10), O2–C–O3 = 121.3 (14), C–O3–O1 = 114.7 (10); O3–O1–Rh = 112.3 (7), O2–C–O4 = 125.6 (16), and O4–C–O3 = 112.9 (13).

Although most of the complexes investigated failed to react with reagent grade CO_2 at ambient conditions, CO_2 fixation was observed to proceed when THF solutions of these compounds were exposed to gas pressures of 30–60 bars for several hours at room temperature. However, of the complexes listed in Table I, $Rh(4\text{-}MeC_6H_4)(bdpp)$[4] only was found to bind carbon dioxide in a reproducible fashion. Elemental analyses of the materials obtained indicated the stoichiometry "$Rh(4\text{-}MeC_6H_4)(bdpp)\cdot CO_4$", suggesting that transformation of the rhodium(I) aryl to a peroxocarbonate of rhodium(III), viz., $Rh(4\text{-}MeC_6H_4)(O_3CO)(bdpp)$ (**1**), had occurred.[5]

1 is practically insoluble in all common hydrocarbons, ethers, alcohols, and ketones. It is readily decomposed by chlorinated solvents such as CH_2Cl_2 and $CHCl_3$. Solution

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[1] Part 18 of the series: "Alkyl and Aryl Compounds of Iridium and Rhodium"; simultaneously part 6 of "Oligophosphine Ligands". For parts 17 and 5, respectively, see ref 4b.

[2] For recent reviews cf.: (a) Ibers, J. A. *Chem. Soc. Rev.* **1982**, *11*, 57. (b) Floriani, C. *Pure Appl. Chem.* **1982**, *54*, 59. (c) Sneeden, R. P. A. In Wilkinson, G., Stone, F. G. A.; Abel, E. W., Eds. "Comprehensive Organometallic Chemistry"; Pergamon Press: Oxford and New York, 1982; Vol. 8, pp 225. (d) Walther, D.; Dinjius, E. *Z. Chem.* **1983**, *23*, 237.

[3] (a) Dahlenburg, L.; Nast, R.; *J. Organomet. Chem.* **1976**, *110*, 395. (b) Dahlenburg, L.; Mirzaei, F.; Yardimcioglu, A. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *37B*, 310.

[4] (a) Arpac, E.; Dahlenburg, L. *J. Organomet. Chem.* **1983**, *241*, 27. (b) Arpac, E.; Dahlenburg, L. *Ibid.* **1983**, *251*, 361. $PhP(CH_2CH_2CH_2PPh_2)_2$ is abbreviated as "bdpp" hereafter.

[5] In a typical experiment carried out under an atmosphere of carbon dioxide (purity ca. 99.5%), a 1-g (1.32-mmol) sample of $Rh(4\text{-}MeC_6H_4)(bdpp)$ was dissolved in 10 mL of THF in a 50-mL Schlenk tube that was subsequently placed into a 250-mL steel autoclave. The vessel was pressurized to 45 bar of CO_2 and the solution stirred for 24 h at room temperature. After the carbon dioxide was vented a lemon yellow powdery precipitate of complex 1 was isolated by addition of hexane and filtration, washed with hexane, and dried in vacuo; yield 813 mg (74%). Anal. Calcd for $C_{44}H_{44}O_4P_3Rh$: C, 63.46; H, 5.33; O, 7.69; P, 11.16; Rh, 12.36. Found: C, 63.55; H, 5.29; O, 8.60; P, 11.05; Rh, 12.41.

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