The chemistry of transition metal carbonyl and phosphine complexes is an important part of organometallic and inorganic chemistry because of relevance to structure and bonding, and to catalytic and stoichiometric organic synthesis. Chiral chelated phosphines are particularly important in application to asymmetric synthesis. Though several articles have been published that deal with the application of infrared spectroscopy to the structure determination of such complexes, experiments combining syntheses with further spectroscopic, synthetic, or kinetic studies are rarer, presumable due to cost, toxicity of the more volatile metal carbonyls, instability towards oxygen, or kinetic inertness, which necessitates long reaction times for thermal substitution. In this experiment, Mo(CO)$_4$(diphos) [diphos = 1,2-bis(diphenylphosphino)ethane] is prepared from diphos and Mo(CO)$_6$ (hexacarbonylmoybdenum(0)) and it is characterized by IR and NMR spectroscopic methods. The experiment additionally illustrates the principles of phase-transfer catalysis. It is based on the literature procedures reported by Shaw and Darensbourg.

Discussion

The probable mechanism of the substitution may be illustrated in the scheme below.

\[
\text{Na}^+ \text{I}^- + \text{Bu}_4\text{N}^+ \text{OH}^- \rightleftharpoons \text{NaOH}^+ \text{Bu}_4\text{N}^+ \text{I}^- \\
\text{H}_2\text{O} \quad \text{toluene} \\
\text{CO} \quad \text{OC} \quad \text{CO} \\
\text{OC} \quad \text{Mo} + \text{Bu}_4\text{N}^+ \text{OH}^- \rightleftharpoons [\text{OC} \quad \text{Mo} \quad \text{CO}] + \text{Bu}_4\text{N}^+ \\
\left[\text{OC} \quad \text{Mo} \quad \text{CO} \right] \quad \text{Bu}_4\text{N}^+ \quad \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2 \\
\left[\text{OC} \quad \text{Mo} \quad \text{CO} \right] \quad \text{Bu}_4\text{N}^+ \quad \text{Ph}_2\text{P} \quad \text{Mo} \quad \text{CO} \quad \text{PPh}_2 \quad \text{Bu}_4\text{N}^+ \quad \text{OH}^- \\
\left[\text{OC} \quad \text{Mo} \quad \text{CO} \right] \quad \text{Bu}_4\text{N}^+ \quad \text{Ph}_2\text{P} \quad \text{Mo} \quad \text{PPh}_2 \quad \text{Bu}_4\text{N}^+ \quad \text{OH}^-
\]

Under phase transfer conditions, the concentration of \(\text{OH}^-\) in the organic phase is small, since \(\text{OH}^-\) is more highly hydrated than \(\text{I}^-\) (\(K_{eq}\) for
Bu₄N⁺OH (org) + I⁻(aq) ⇌ Bu₄NI (org) + OH⁻(aq)

is about 100)⁶. This minimizes decarboxylation of the M–COOH intermediate in the presence of excess OH⁻. The COOH group has been well characterized as a cis-labilizing ligand⁷, and labeling experiments also suggest a direct involvement of the incoming phosphine ligand in the labelization to ¹³CO or ¹⁸OH⁻ exchange under phase transfer conditions⁸.

The C₃ᵥ symmetry of the cis-M(CO)₄L₂ complex is amply demonstrated by the observation of four infrared bands (2a₁+b₁+b₂)⁸ (2025, 1932, 1920, 1906 cm⁻¹).

NMR spectroscopy may also be used in spectroscopic characterization, though care must be taken in oversimplification. Neglecting the phenyl multiplet at 7.3-7.7 ppm, the methylene protons may be treated approximately as the X part of an AXX'X''X'''A' system. The spectrum consists of a fairly sharp doublet of separation 18 Hz equivalent to |²J_P⁺₃J_P⁻| superimposed on a broad symmetrical base lying mainly to the outside of the doublet⁹. The crystal structure of Mo(CO)₆(diphos) has been reported¹⁰. It illustrates the puckered nature of the chelate ring and the distortion from octahedral geometry (< P–Mo–P = 80°), and the longer Mo–C distance (2.04 Å) for the mutually trans carbonyl ligands compared to the pair that are trans to phosphorous (1.99 Å), consistent with the poorer π-acceptor capacity of phosphorous.

Experimental procedure

Caution: All metal carbonyl complexes must be regarded as toxic because of their liberation of CO on decomposition or reaction. Mo(CO)₆ and Mo(CO)₄(diphos) are relatively nonvolatile, but all manipulations must be done in a fume hood. Particularly avoid breathing any dust from Mo(CO)₆, diphos, or tetrabutylammonium iodide. Any solid spillages must be swept up and placed in disposal bags.

Place Mo(CO)₆ (0.10 g, 0.38 mmole), diphos (0.15 g, 0.37 mmole), toluene (7 mL), 50% NaOH solution (1.0 mL) and tetrabutylammonium iodide (0.010 g, 0.020 mmole) in a 10-mL round-bottomed flask fitted with a magnetic stirring bar and a small condenser. After the solution is degassed with N₂ for 5 minutes, keep the flask under a positive pressure of N₂ and heat to 80 °C with stirring for 2 hours. After cooling, separate the organic and aqueous layers and reduce the organic layer to about one-quarter of its original volume using N₂. Add ethanol (2 mL) and separate the crude product by filtration through a Hirsh funnel. The yield at this stage is about 0.16 g (73%). The compound may be recrystallized for IR analysis by dissolving in a minimum amount of CH₂Cl₂ (ca. 5 mL), filtering (if necessary), adding of an equal volume of methanol, and cooling in an ice bath for 2 hours. The white crystals are isolated by filtration (mp with decomposition 186-188 °C). Though the substitution is conducted under N₂, reactants and products are sufficiently stable in air for the purposes of this experiment.

References
