# Monocyclopentadienyl Complexes of Niobium(III) and Tantalum(III). Structures of $[Cp'NbCl(CO)_2]_2(\mu\text{-}Cl)_2$ and $Cp'NbCl_2(ArCCAr)$ (Ar = *p*-Tolyl)

M. David Curtis,* Julio Real, and Daekeun Kwon

*Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109-1055*

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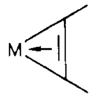
The compounds $[Cp^RMCl(\mu\text{-}Cl)(CO)_2]_2$ (**1**, R = H ($C_5H_5$), **1a**, R = Me ($C_5H_4Me$), M = Nb; **2**, R = H, M = Ta) were prepared by the Al reduction of $Cp^RMCl_4$ under CO. Internal alkynes displace two CO ligands to give complexes of the type $CpM(RCCR)Cl_2$. Phosphines displace only one CO group and form compounds, e.g., $CpNbCl_2(CO)(PMe_3)_2$. A tris(phosphine) complex, $CpTaCl_2(PMe_3)_2$, was prepared by reduction of $CpTaCl_4$ by Na/Hg in the presence of $Me_3P$. Acrylate esters displace CO to give metallacycles, $CpNb(CH_2CHC(OR)O)Cl_2$. Likewise, butadiene displaces both carbonyls from $Cp^*Ta(CO)_2Cl_2(THF)$ with the formation of the previously reported tantalacyclopentene, $Cp^*Ta(CH_2CHCHCH_2)Cl_2$ ($Cp^*$ = $C_5Me_5$). The niobium alkyne adduct $Cp'NbCl_2$(tolan) was also prepared by direct reduction of $Cp'NbCl_4$ with Al in the presence of the alkyne. An EHMO analysis revealed that the alkyne adducts are best viewed as Nb(V) metallacyclopropenes with additional donation of electron density from $\pi_\perp$ (see A below). The



A

EHMO analysis also explained why the alkyne adducts form stable 16e complexes, whereas phosphines add an additional ligand to form 18e complexes. The structures of **1a** and $Cp'NbCl_2$(tolan) (**3c**) were determined by single-crystal X-ray diffractometry. **1a**: $a$ = 7.117 (1) Å, $b$ = 11.902 (2) Å, $c$ = 11.892 (2) Å, $\beta$ = 101.79 (1)° space group $P2_1/c$, $Z$ = 2, $V$ = 986.0 (2) Å$^3$, $\rho_{calcd}$ = 2.01 g/mL, $R$ = 0.027, $R_w$ = 0.038 based on 1965 reflections with $I > 3\sigma(I)$. **3c**: $a$ = 9.793 (3) Å, $b$ = 13.353 (3) Å, $c$ = 15.677 (4) Å, $\beta$ = 93.15°, space group $P2_1/n$, $Z$ = 4, $V$ = 2047 (1) Å$^3$, $\rho_{calcd}$ = 1.46 g/mL, $R$ = 0.037, $R_w$ = 0.036 based on 1999 reflections with $I > 3\sigma(I)$.

## Introduction

In comparison with bis(cyclopentadienyl) complexes of Nb and Ta, the chemistry of monocyclopentadienyl derivatives of these early transition metals is much less developed. This situation is due in part to the lack of readily available starting materials. Only high-pressure routes to $CpM(CO)_4$ (M = Nb, Ta) via $M(CO)_6^-$ or reductive carbonylation of $CpMCl_4$ were known prior to 1983.[1-4] Even the syntheses of $CpMCl_4$ were inefficient until it was discovered that $Bu_3SnCp$ effectively transfers the Cp group to high-valent metal chlorides without concomitant reduction of the metal.[5-7]

In 1980, a low-pressure, reductive carbonylation of $CpMCl_4$ was reported to give "$CpMCl_2(CO)_3$".[8] In the same year, Herrmann et el. obtained an incompletely characterized $CpTaCl_x(CO)_y$.[9] In a preliminary communication, we have reported that the Nb complex is actually a dicarbonyl dimer, $[CpNbCl_2(CO)_2]_2$ (**1**).[10] Herrmann's material most likely has a similar structure.

We have continued to develop the chemistry of **1** and its Ta analogues along the lines of (1) CO displacement reactions, (2) chloride replacement reactions, and (3) reductive coupling. This report will focus on CO displacement chemistry and the structural details of **1** and $CpNbCl_2(ArC{\equiv}CAr)$ (Ar = *p*-tolyl). Results of an EHMO study of the alkyne complex are also discussed.

## Experimental Section

All reactions and manipulations were carried out under a $N_2$ atmosphere in an inert-atmosphere box or with Schlenk techniques. Niobium and tantalum pentahalides were purchased from Pressure Chemicals Co., Pittsburgh, PA 15201, and stored in the inert-atmosphere box (note: pentahalides will absorb and react with solvent vapors present in the box atmosphere unless kept in tightly capped containers).

$CpMCl_4$ (M = Nb, Ta) were prepared from $MCl_5$ and $Bu_3SnCp$ as described previously.[5-7] NMR spectra were obtained on a Bruker WM-360 (360 MHz $^1H$, 90.56 MHz $^{13}C$) or a Bruker AM-300 (300 MHz $^1H$, 75.5 MHz $^{13}C$) spectrometer at ambient temperatures (ca. 22 °C for $^1H$, 30 °C for $^{13}C$ spectra. IR spectra were recorded on a Perkin-Elmer 1330 instrument calibrated with polystyrene film. Mass spectra were obtained on a Finnegan 4021 spectrometer using the heated probe for volatilization and either CI (methane) or EI for ionization of the sample. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory or Galbraith Labs, Inc.

**$[CpNbCl(CO)_2]_2(\mu\text{-}Cl)_2$ (1).** A 500-mL Schlenk flash was charged in the inert atmosphere box with 16.0 g (53.3 mmol) of $CpNbCl_4$, 2.0 g (74 mmol, excess) of clean Al powder, (0.01–0.10 g, 0.04–0.40 mmol) of $HgCl_2$, and a stirring bar. The flask was transferred to a Schlenk line, and 200 mL of THF, freshly distilled from K–benzophenone, was added. The brick red $CpNbCl_4$ turned

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pink and partially dissolved to give a pink solution. The $N_2$ branch of the Schlenk line was then connected to a cylinder of CO (CP grade) and the mixture stirred for 48 h under a CO atmosphere while being protected from laboratory light with an aluminum foil wrapping around the flask. At the end of this time, an orange solid had formed and the color of the solution was deep cherry red. The mixture was then cooled to −10 °C, and the solids were collected by filtration, washed with three, 10-mL portions of ethyl ether (freshly distilled from K–benzophenone), and dried under vacuum. The mother liquor and washings were saved for further treatment.

The orange solid was dissolved in 400–600 mL of THF and the solution filtered to remove excess Al. The red filtrate was concentrated under vacuum to a volume of ca. 50 mL and an equal volume of hexane added. This mixture was cooled to −10 °C to crystallize the product (crystallization may be induced by scratching the flask). The orange crystals were collected by filtration and washed with 3 × 5-mL portions of ether. The filtrate was concentrated further, and more hexane was added to give a second crop of product (7.9 g, both crops). A third crop (2.9 g) was obtained from the original mother liquor by concentration to a volume of ca. 40 mL, adding 20 mL of hexane, cooling to −10 °C, and washing the resultant crystals with 10 × 6 mL portions of ether to remove residual $AlCl_3$. Overall yield: 10.8 g (70%) of microcrystalline **1**.

The methylcyclopentadienyl derivative $[Cp'NbCl(CO)_2]_2(\mu\text{-}Cl)_2$ (**1a**), may be obtained in an equally high yield from $Cp'NbCl_4$ with the procedure described above.

Compounds **1** and **1a** are soluble in THF and easily form supersaturated solutions in this solvent. The compounds are sparingly soluble in ether, toluene, benzene, and methylene chloride and are more soluble in coordinating solvents, e.g. acetonitrile and acetone in which decomposition occurs in a few hours. In solution, the compounds are heat and light sensitive, decomposing with loss of CO to give paramagnetic clusters.[11]

**1**: $^1H$ NMR ($C_7D_8$) $\delta$ 4.28; $^1H$ NMR ($CD_3CN$) $\delta$ 5.44, 5.46, 5.21 (intensity ratio 25:10:65); IR (Nujol) $\nu_{CO}$ 2025 (s), 1955 (sh), 1940 (s); IR (THF) $\nu_{CO}$ 2040 (s), 1955 (s) cm$^{-1}$. Anal. Found (Calcd for $C_{14}H_{10}Cl_4Nb_2O_4$): C, 29.36 (29.51); $^1H$, 1.95 (1.77); Cl, 25.14 (24.89).

**1a**: $^1H$ NMR ($CD_3CN$) $\delta$ 5.30, 5.15, 4.95 (multiplets, intensity ratio 20:20:20), 2.15, 2.08 (singlets, intensity ratio 13:27); IR (Nujol) $\nu_{CO}$ 2025 (s), 1955 (sh), 1940 (s); IR (THF) $\nu_{CO}$ 2040 (s), 1955 (s) cm$^{-1}$. Anal. Found (Calcd for $C_{16}H_{14}Cl_4Nb_2O_4$): C, 32.49 (32.14); H, 2.64 (2.36); Cl, 23.66 (23.72).

**$[CpTaCl(CO)_2]_2(\mu\text{-}Cl)_2$ (2).** In a 400-mL, thick-walled pressure flask equipped with a stainless-steel head fitted with gas-inlet needle valves and a pressure gauge was placed 9.0 g (23.2 mmol) of bright yellow $CpTaCl_4$, 1.0 g (37.0 mmol, excess) Al powder, 0.5 g (1.8 mmol) of $HgCl_2$, a large magnetic stirring bar, and 250 mL of THF ($N_2$ atmosphere). Upon addition of the THF, the solid turned apple green and partially dissolved to give a pale, apple green solution. The flask was removed from the inert atmosphere box and pressurized (40 psi) with CO. The mixture was stirred vigorously at room temperature for 11 h, after which time a viscous, deep orange solution had formed. The excess Al powder was removed with difficulty by filtration through a 2 cm layer of Celite in a large, fritted funnel (inert-atmosphere box). The thick, orange-red filtrate was concentrated under vacuum to a red oil. The oil was stirred thoroughly with 100 mL of ether, and vigorous scratching of the flask induced crystallization. The solid was collected by filtration, washed with 5 × 3 mL portions of ether and 4 × 3 mL portions of methylene chloride, and dried under vacuum. A second crop of product was obtained from the ether mother liquor by concentration and cooling to −10 °C. Combined yield: 2.7 g (31%) of bright orange, microcrystalline **2**.

**2**: $^1H$ NMR ($C_7D_8$) $\delta$ 4.85; $^1H$ NMR ($CD_3CN$) $\delta$ 5.40, 5.25 (singlets, intensity ratio 13:1); IR (THF) $\nu_{CO}$ 2030 (s), 1935 (s) cm$^{-1}$. Anal. Found (Calcd for $C_{14}H_{10}Cl_4O_4Ta_2$): C, 22.71 (22.54); H, 1.46 (1.35); Cl, 19.26 (19.01).

**$RNbCl_2(ArC{\equiv}CAr)$ [R = Cp, Ar = *p*-Tolyl (3a); R = Cp, Ar = Phenyl (3b); R = Cp′, Ar = *p*-Tolyl (3c); R = Cp′, Ar = Phenyl (3d).** Two procedures for the synthesis of these derivatives were developed. Procedure A was used only for **3c**. Procedure B is more simple, gives excellent yields for all derivatives, and is recommended.

(A) A 250-mL flask was charged with 2.30 g (7.28 mmol) of $Cp'NbCl_4$, 1.50g (7.28 mmol) of di-*p*-tolylacetylene, 0.40 g (15 mmol, excess) of Al powder, 0.10 g (0.4mmol) of $HgCl_2$, and 100 mL of THF. The mixture was stirred for 6 h to give a deep red solution. The excess Al was removed by filtration through a 2-cm bed of Celite on a fritted funnel. The solvent was removed under vacuum from the filtrate to give a red, oily residue which was dissolved in toluene (40–50 mL). The toluene was then stripped under vacuum. The process of dissolving the residue in toluene and then taking the solution to dryness under vacuum was repeated three times to remove residual THF which may be coordinated to the product. The residue remaining from the third cycle was dispersed in 40 mL of *n*-butyl ether; scratching the walls of the flask with a spatula caused **3c** to crystallize. The red crystals were collected, washed with *n*-butyl ether (3 × 5 mL) and then hexane (2 × 5 mL), and vacuum dried. Yield: 2.30 g (70%) of red, crystalline **3c**.

(B) $[CpNbCl(CO)_2]_2(\mu\text{-}Cl)_2$ (1.00 g, 1.75 mmol) was dissolved in 80 mL of THF. To this solution was added 0.73 g (3.5 mmol) of solid di-*p*-tolylacetylene with rapid stirring. Gas evolution was noted and the color of the solution deepened. The mixture was evaporated to dryness under vacuum, and the residue was taken up in toluene and then dried three times as above to remove traces of THF. The residue from the final cycle was dissolved in toluene and filtered through a 2-cm bed of Celite, and the deep red filtrate was concentrated to a volume of ca. 5 mL. Hexane (5 mL) was added dropwise until crystallization commenced, at which point an additional 20 mL of hexane was added. The red crystalline product was collected, washed with hexane (3 × 5 mL), and dried under vacuum. Yield: 1.45 g (95%). Derivatives **3b**, **3c**, and **3d** were obtained by identical procedures.

**3a**: $^1H$ NMR ($C_6D_6$) $\delta$ 2.11 (s, 6 H, Ar $CH_3$), 5.80 (s, 5 H, Cp), 7.06, 7.63 (dd, $J$ = 8 Hz, 8 H, $C_6H_4Me$); $^{13}C$ NMR ($C_6D_6$) $\delta$ 21.4 ($ArCH_3$), 112.4 (Cp), 129.6, 130.0, 136.5, 139.9 ($C_6H_4Me$), 216.1 ($C{\equiv}C$). Anal. Found (Calcd for $C_{21}H_{19}Cl_2Nb$): C, 57.78 (57.96); H, 4.21 (4.40); Cl, 16.12 (16.29).

**3b**, **3c**, and **3d** showed similar spectral parameters and gave excellent elemental analyses.

**$CpNbCl_2(EtC{\equiv}CEt)$ (3e).** To a solution of $[CpNbCl(CO)]_2(\mu\text{-}Cl)_2$ (0.70 g, 1.23 mmol) in 30 mL of THF was added 0.20 g (2.5 mmol) of 3-hexyne. Gas evolution commenced immediately, and the color of the solution darkened. After the solution stirred at room temperature for 4 h, the THF was removed under vacuum and residue taken up in 20 mL of hexane. This mixture was filtered through a bed of Celite to remove a small amount of purple solid. The deep red filtrate was concentrated to a volume of 5 mL and cooled to −8 °C. The resulting brick-red crystals were collected by filtration and dried under vacuum: yield 0.63 g (83%); $^1H$ NMR ($C_6D_6$) $\delta$ 5.7 (s, 5 H, Cp), 2.97 (q, $J$ = 7.5 Hz, 4 H, $CH_2$), 1.07 (t, $J$ = 7.5 Hz, 6 H, $CH_3$). Anal. Found (Calcd for $C_{11}H_{15}Cl_2Nb$): C, 42.58 (42.47); H, 4.86 (4.85); Cl, 23.18 (22.79).

**$CpTaCl_2(ArC{\equiv}CAr)$ [Ar = *p*-Tolyl (4a); Ar = Phenyl (4b)].** These compounds were prepared by procedure b as described above. From 1.11 g (1.49 mmol) of **2** and 0.62 g (3.01 mmol) of di-*p*-tolylacetylene in 80 mL of THF was obtained 1.44 g (92%) of orange-red, crystalline **4a**. Equally good yields of **4b** were obtained from **2** and diphenylacetylene.

**4a**: $^1H$ NMR ($C_6D_6$) $\delta$ 2.15 (s, 6 H, $ArCH_3$), 5.68 (s, 5 H, Cp), 7.11, 7.64 (dd, $J$ = 8 Hz, 8 H, $C_6H_4Me$); $^{13}C$ NMR ($C_6D_6$) $\delta$ 21.4 ($ArCH_3$), 110.8 (Cp), 129.5, 130.6, 139.4, 139.8 ($C_6H_4Me$), 221.0 ($C{\equiv}C$). Anal. Found (Calcd for $C_{21}H_{19}Cl_2Ta$): C, 47.86 (48.21); H, 3.79 (3.66); Cl, 13.25 (13.55).

Similar spectra properties were obtained for **4b**.

**Reaction of $[CpNbCl(CO)_2]_2(\mu\text{-}Cl)_2$ with Acetylene.** Acetylene was bubbled through a solution of 0.12 g (0.21 mmol) of $[CpNbCl(CO)]_2(\mu\text{-}Cl)_2$ in 30 mL of THF. A rapid, exothermic reaction ensued, and the color of the solution changed from light, red-orange to purple-black. After 20 min, the THF solution set to a gel. The flask was evacuated, causing the gel to shrink and finally collapse to silvery-black flakes of polyacetylene. The polymer is extremely air-sensitive and insoluble in all common solvents. Total weight: 600 mg (480 mg of polymer, which

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corresponds to an average degree of polymerization, DP = 88). IR (KBr): 3010 (m), 1398 (m), 1012 (m) $cm^{-1}$, which corresponds to a mixture of *cis*- and *trans*-polyacetylene.[12]

**Reaction of $[CpNbCl(CO)_2]_2(\mu\text{-}Cl)_2$ with Excess Phenylacetylene.** Phenylacetylene (9.7 g, 95 mmol) was added to 50 mg (0.087 mmol) of $[CpNbCl(CO)_2]_2(\mu\text{-}Cl)_2$ dissolved in 10 mL of THF. This solution was heated to reflux for 24 h, during which time the solution became very viscous. Upon cooling to room temperature, the mixture solidified to a hard mass. The solid was dissolved in benzene (50 mL), and the resulting solution was filtered, concentrated, and layered with hexane to give a pale yellow solid identified as 1,3,5-triphenylbenzene (mp 172 °C; $m/z$ = 306; IR (KBr) 3059, 3033, 1652, 751, 701 $cm^{-1}$).[13] A second crop appeared to be contaminated with the 1,2,4-isomer (mp 100 °C; $m/z$ = 306). Yield: 8.5 g (88% of initial alkyne).

**$CpNbCl_2(PMe_3)_2(CO)$ (5).** A 100-mL side-arm flask was loaded with 0.10 g (0.18 mmol) of $[CpNbCl(CO)_2]_2(\mu\text{-}Cl)_2$ and 30 mL of THF. Trimethylphosphine (0.2 mL, 1.9 mmol, precooled to −40 °C) was added dropwise. The color of the solution slowly changed from brick-red to pink-red. At the end of 4 h, the $\nu_{CO}$ bands of the starting material had disappeared in the IR spectrum. The THF was removed under vacuum, and the red, solid residue was dissolved in $CH_2Cl_2$. This solution was filtered, and the filtrate was concentrated and layered with hexane to give red crystals. The product was collected by filtration and dried under vacuum: yield 0.10 g (70%); $^1H$ NMR ($C_6D_6$) $\delta$ 4.52 (t, $J_{PH}$ = 2.5 Hz, 5 H, Cp) 1.13 (pseudo-t, $J_{PH}$ = 3.65, 4.08 Hz, 18 H, $PMe_3$); $^1H$ NMR ($CD_2Cl_2$) 4.96 (t, $J_{PH}$ = 2.5 Hz, 5 H, Cp), 1.40 (pseudo-t, $J_{PH}$ = 3.9 Hz, 18 H, $PMe_3$); IR (THF) $\nu_{CO}$ 1924 $cm^{-1}$. These properties are identical with those reported earlier.[14]

The reaction of 1 with DPPE appears to give a similar adduct, $CpNbCl_2(CO)(DPPE)$, but pure product has not been obtained due to the poor solubility of the adduct.

**$CpTa(PMe_3)_3Cl_2$ (6).** Sodium amalgam (6.8 mL, 0.5% Na, 20 mmol) and ca. 50 mL of toluene were cooled to −40 °C, and 2.1 mL (20 mmol) of trimethylphosphine (previously cooled to −40 °C) was added dropwise with a syringe. $CpTaCl_4$ (3.87 g, 10 mmol) was added with rapid stirring and the suspension allowed to warm to ambient temperature. The solution turned yellow, then gray, and finally burgundy red after 1–2 h. The solids were allowed to settle, and the supernate was filtered through a bed of Celite. Hexane was added slowly to the filtrate to give the red, crystalline product (40% yield): MS $m/z$ 468 ($P^+ - PMe_3$), 392 ($P^+ - 2PE_3$), 316 ($P^+ - 3PMe_3$); $^1H$ NMR $\delta$ 4.13 (q, $J_{PH} \simeq$ 3 Hz), 1.19 (t, $J_{PH}$ = 3.3 Hz), 1.11 (d, $J_{PH}$ = 6.6 Hz). Anal. Found (Calcd for $C_{14}H_{32}Cl_2P_3Ta$): C, 30.10 (30.84); H, 5.73 (5.91); Cl, 13.34 (13.00).

**$Cp^*TaCl_2(C_4H_6)$.** A 100-mL side-arm flask was loaded with 0.3 g (0.7 mmol) of $Cp^*TaCl_2(CO)_2(THF)$ in 30 mL of THF. Butadiene was then bubbled through the solution, the color of which changed from orange to purple in 5 h. The THF was evaporated under vacuum and the solid residue dissolved in 30 mL of toluene. This solution was filtered and concentrated to a volume of ca. 5 mL and cooled to −8 °C. The purple crystals that formed were collected by filtration, washed with cold hexane (2 × 5 mL), and dried under vacuum to yield 0.23 g (90%) of product: $^1H$ NMR ($C_6D_6$) $\delta$ 7.05 (m, 2 H), 1.8 (s, 15 H), 0.81 (m, 2 H), −0.13 (m, 2 H). These parameters are identical with those reported.[15]

**$CpNbCl_2(CH_2CHCO_2R)$ [R = Me (7a), Et (7b), Bu (7c)].** To 0.22 g (0.37 mmol of $[CpNbCl_2(CO)_2]_2$ dissolved in 15 mL of THF was added 0.20 g (2.3 mmol) of methyl acrylate. The mixture was stirred until the $\nu_{CO}$ bands of the starting material disappeared (20 h), after which time a yellow solid had precipitated. The solid was recovered by filtration, washed with cold THF (2 × 5 mL) and hexane (3 × 5 mL), and dried under vacuum: yield 0.19 g (80%), IR (KBr) 1731, 1617, 1520 $cm^{-1}$; $m/z$ = 314 ($P^+$), 279 ($P - Cl)^+$, 259 $(CpNbCl_2OMe)^+$, 228 $(CpNbCl_2)^+$. Anal. Found (Calcd for $C_9H_{11}Cl_2NbO_2$): C, 33.44 (34.32); H, 3.47 (3.52); Cl, 22.89 (22.51).

**Table I. Crystallographic Statistics**

| | $[Cp'NbCl(\mu\text{-}Cl)(CO)_2]_2$ (1a) | $Cp'NbCl_2(ArCCAr)$ (3c) |
|---|---|---|
| formula, MW | $C_{16}H_{14}Cl_4Nb_2O_4$, 598 | $C_{22}H_{21}Cl_2Nb$, 449 |
| $a, b, c$, Å | 7.117 (1), 11.902 (2), 11.892 (2) | 9.793 (3), 13.353 (3), 15.677 (4) |
| $\beta$, deg | 101.79 (1) | 93.15 (2) |
| $Z, V$, Å$^3$ | 2; 986.0 (2) | 4; 2047 (1) |
| $\rho_{calcd}$, g/cm$^3$ | 2.01 | 1.46 |
| space group | $P2_1/c$ | $P2_1/n$ |
| cryst dimens, mm | 0.211 × 0.110 × 0.120 | ca. 0.3 × 0.3 × 0.3 |
| radiatn; λ, (Å) | Mo K$\bar{\alpha}$, 0.71069 | Mo K$\bar{\alpha}$, 0.71069 |
| monochromator | graphite cryst | graphite cryst |
| $\mu$, cm$^{-1}$ | 16.8 | 8.28 |
| scan speed, deg/min | 2.5–12.0 (variable) | 2.5–12.0 (variable) |
| scan range | Mo K$\bar{\alpha}$ − 0.9 to Mo K$\bar{\alpha}$ + 0.9 | Mo K$\bar{\alpha}$ − 0.8 to Mo K$\bar{\alpha}$ + 0.8 |
| bkgd: scan time | 0.8 | 0.8 |
| std reflctns | 311, 141, 104 | 31$\bar{1}$, 118, 190 |
| $2\theta$ limit, deg | 50 | 45 |
| reflctns | 2110 (1365 with $I > 3\sigma$) | 3019 (1999 with $I > 3\sigma$) |
| $N_o/N_v$ | 11.6 | 8.9 |
| GOF | 1.32 | 1.57 |
| $R$, $Rr_w$ | 0.027, 0.038 | 0.037, 0.036 |
| largest residual, e Å$^{-3}$ | 0.34 | 0.42 |

**Table II. Fractional Atomic Coordinates for $[Cp'NbCl(CO)_2]_2(\mu\text{-}Cl)_2$ (1a)**

| Atom | $x$ | $y$ | $z$ | $B$,[a] Å$^2$ |
|---|---|---|---|---|
| Nb | 0.10020 (5) | 0.07476 (3) | 0.15254 (3) | 2.18 (1) |
| Cl1 | 0.13019 (15) | 0.41434 (9) | 0.43817 (9) | 2.06 (2) |
| Cl2 | −0.19066 (17) | 0.19134 (10) | 0.07971 (10) | 2.5 (2) |
| O7 | 0.2365 (6) | 0.3345 (3) | 0.1870 (3) | 3.62 (10) |
| O8 | −0.1064 (6) | 0.1060 (4) | 0.3686 (3) | 4.11 (9) |
| C1 | 0.3566 (6) | 0.0669 (4) | 0.3161 (4) | 2.38 (9) |
| C2 | 0.2614 (7) | 0.9614 (4) | 0.3068 (5) | 2.56 (9) |
| C3 | 0.2902 (7) | 0.9061 (4) | 0.2069 (5) | 2.67 (11) |
| C4 | 0.3974 (7) | 0.9770 (5) | 0.1517 (5) | 2.87 (10) |
| C5 | 0.4373 (7) | 0.0758 (5) | 0.2167 (5) | 2.84 (9) |
| C6 | 0.3915 (11) | 0.1423 (6) | 0.4190 (6) | 4.09 (13) |
| C7 | 0.1919 (7) | 0.2433 (4) | 0.1771 (4) | 2.57 (10) |
| C8 | −0.0358 (7) | 0.0941 (4) | 0.2923 (4) | 2.61 (10) |

[a] Equivalent isotropic $B$ value.

The ethyl and butyl acrylate adducts were prepared in an identical manner in the hopes of obtaining more soluble complexes. However, all these acrylate adducts are only sparingly soluble in common solvents. Analytical and spectral data for R = Et: IR (KBr) 1721, 1630 $cm^{-1}$; $m/z$ = 328 ($P^+$), 298 $(P - Cl)^+$, 273 $(CpNbCl_2OEt)^+$, 228 $(CpNbCl_2)^+$. For R = Bu: IR (KBr) 1725, 1618, 1503 $cm^{-1}$; $m/z$ = 356 ($P^+$), 321 $(P - Cl)^+$, 301 $(CpNbCl_2OBu)^+$, 228 $(CpNbCl_2)^+$. Anal. Found (Calcd for $C_{12}H_{17}Cl_2NbO_2$): 38.15 (40.36); H, 4.54 (4.80); Cl, 20.08 (19.86). Note: considerable difficulty was occasionally experienced in obtaining reliable carbon analyses on Nb and Ta complexes, possibly due to metal carbide formation during combustion.

**X-ray Structure Determinations.** Data were collected on a Syntex $P2_1$ diffractometer (see Table I for statistics). Two software packages were used in the solution and refinement: X-RAY[16] and SHELX.[17] In both sets of programs, the function $\sum w\,(|F_o| - |F_c|)^2$ was minimized, where $w$ = weighting factor. In

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[13] *Dictionary of Organic Compounds*, 5th Ed.; Chapman and Hall: New York, 1982, Vol. 5, p 5613.

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[16] The XRAY76 package contains the following programs: SYNCOR (W. Schmonsees—data reduction), FORDAP (A. Zalkin—Fourier synthesis), ORFLS (W. R. Busing, K. O. Martin, H. A. Levy—least-squares refinement), ORFFE (W. R. Busing, K. O. Martin, H. A. Levy—bond distances, errors, and standard deviations), HFINDR (A. Zalkin—calculated H-atom positions), ABSORB (D. Templeton and L. Templeton—numerical absorption correction), and MULTAN78 (P. Main—direct methods).

[17] SHELX (C. M. Sheldrick) includes routines for direct methods, Fourier synthesis, least-squares refinements, numeric absorption corrections, calculations of bond distances and angles, and standard deviations.

**Table III. Selected Bond Distances (Å) and Angles (deg) for $[Cp'NbCl(\mu\text{-}Cl)(CO)_2]_2$ (1a)**

| Bond Distances | | | |
|---|---|---|---|
| Nb···Nb | 4.031 (1) | Nb–C(CO) | 2.11 (1) (av) |
| Nb–Cl1 | 2.603 (1) | C–O | 1.127 (6) (av) |
| Nb–Cl1′ | 2.605 (1) | Nb–C(Cp) | 2.39 (3) (av) |
| Nb–Cl2 | 2.495 (1) | Cl1···Cl1′ | 3.297 (2) |
| **Bond Angles** | | | |
| Cl1–Nb–Cl1′ | 78.55 (4) | Cl1–Nb–C7 | 90.2 (1) |
| Nb′–Nb–Cl2 | 79.46 (3) | Cl1–Nb–C8 | 155.7 (1) |
| Nb–Cl1–Nb′ | 101.45 (4) | C7–Nb–C8 | 88.1 (2) |
| Nb–C7–O7 | 177.5 (4) | Nb–C8–O8 | 178.5 (5) |
| Cl2–Nb–C7 | 74.4 (1) | Cl2–Nb–Cl1 | 81.7 (4) |

**Table IV. Fractional Atomic Coordinates for $Cp'NbCl_2(ArCCAr)$ (Ar = *p*-Tolyl, 3c)**

| atom | $x$ | $y$ | $z$ | $U$, Å$^2$ |
|---|---|---|---|---|
| Nb | 0.3563 (1) | 0.1145 (0) | 0.1876 (0) | 0.0424 |
| Cl1 | 0.4040 (2) | 0.1276 (1) | 0.0418 (1) | 0.0639 |
| Cl2 | 0.3024 (2) | 0.2828 (1) | 0.2150 (1) | 0.0672 |
| C10 | 0.1661 (5) | 0.0655 (4) | 0.2199 (4) | 0.0420 |
| C20 | 0.2000 (5) | 0.0148 (4) | 0.1530 (3) | 0.0387 |
| C11 | 0.0647 (6) | 0.0692 (4) | 0.2856 (3) | 0.0433 |
| C12 | 0.0688 (7) | 0.1448 (5) | 0.3461 (4) | 0.0629 |
| C13 | −0.0218 (8) | 0.1448 (5) | 0.4110 (4) | 0.0749 |
| C14 | −0.1165 (6) | 0.0710 (5) | 0.4181 (4) | 0.0559 |
| C15 | −0.1207 (6) | −0.0041 (5) | 0.3576 (4) | 0.0595 |
| C16 | −0.0315 (6) | −0.0057 (4) | 0.2917 (3) | 0.0518 |
| C17 | −0.2128 (7) | 0.0709 (6) | 0.4896 (4) | 0.0792 |
| C21 | 0.1569 (6) | −0.0638 (4) | 0.0936 (3) | 0.0373 |
| C22 | 0.0194 (6) | −0.0870 (4) | 0.0762 (3) | 0.0429 |
| C23 | −0.0181 (6) | −0.1620 (5) | 0.0180 (4) | 0.0495 |
| C24 | 0.0796 (7) | −0.2157 (4) | −0.0237 (4) | 0.0504 |
| C25 | 0.2161 (7) | −0.1926 (5) | −0.0058 (4) | 0.0590 |
| C26 | 0.2537 (5) | −0.1160 (5) | 0.0497 (4) | 0.0496 |
| C27 | 0.0377 (7) | −0.2974 (5) | −0.0860 (5) | 0.0754 |
| Cp1 | 0.5862 (7) | 0.1202 (6) | 0.2570 (5) | 0.0653 |
| Cp2 | 0.4929 (8) | 0.1141 (6) | 0.3208 (4) | 0.0741 |
| Cp3 | 0.4282 (7) | 0.0213 (7) | 0.3112 (5) | 0.0767 |
| Cp4 | 0.4788 (8) | −0.0280 (5) | 0.2415 (5) | 0.0746 |
| Cp5 | 0.5774 (7) | 0.0331 (6) | 0.2081 (4) | 0.0688 |
| Cp6 | 0.6743 (9) | 0.2079 (8) | 0.2467 (6) | 0.1227 |

**Table V. Selected Bond Distances (Å) and Angles (deg) for $Cp'NbCl_2(ArCCAr)$ (Ar = *p*-Tolyl, 3c)**

| Bond Distances | | | |
|---|---|---|---|
| Nb–Cl1 | 2.365 (2) | C10–C20 | 1.307 (7) |
| Nb–Cl2 | 2.353 (2) | C10–C11 | 1.470 (7) |
| Nb–C10 | 2.063 (5) | C20–C21 | 1.449 (7) |
| Nb–C20 | 2.079 (5) | C–C(Cp) | 1.392 (3) (av) |
| Nb–C(Cp) | 2.41 (3) | C–C(ar) | 1.38 (1) (av) |
| Cp1–Cp6 | 1.47 (1) | C(Ar)–Me | 1.505 (8) (av) |
| **Bond Angles** | | | |
| Cl1–Nb–Cl2 | 99.4 (1) | C10–Nb–C20 | 36.8 (2) |
| Cl2–Nb–C10 | 92.5 (2) | Nb–C10–C11 | 144.5 (4) |
| Cl1–Nb–C10 | 119.3 (2) | Nb–C20–C21 | 144.6 (4) |
| Cl1–Nb–C20 | 88.6 (1) | Nb–C10–C20 | 72.3 (3) |
| Cl2–Nb–C20 | 119.3 (2) | Nb–C20–C10 | 70.9 (3) |

the X-RAY package, $w = 4F_o^2/(\sigma^2(F_o^2) + 0.0016F_o^4)$, and in SHELX, $w = 1/(\sigma^2(F_o) + 10^{-4}F_o^2)$. Conventional agreement indices $R$ and $R_w$ and "goodness of fit" = $[w(|F_o| - |F_c|)^2]^{1/2}/(N_o - N_v)^{1/2}$ ($N_o$ and $N_v$ = number of observed reflections and number of variables, respectively) were used throughout. Scattering factors were taken from ref 18.

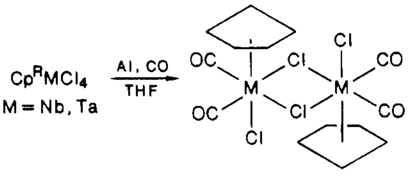
Crystals of $[Cp'NbCl(CO)_2]_2(\mu\text{-}Cl)_2$ (**1a**) were grown under an inert atmosphere from a THF solution layered with hexane. A suitable crystal was sealed in a thin-walled glass capillary and mounted on the diffractometer. Cell constants were determined from 15 centered reflections.

Following data reduction, the metal atoms were located from a Patterson map and subsequent difference maps revealed the location of all non-hydrogen atoms. These were refined anisotropically to convergence. H atoms were inserted at calculated positions with fixed temperature factors ($d$(C – H) = 1.10 Å; $B_H = 1.2B_c$, where $B_c$ = isotropic temperature factor of the C atom to which the H atom is bonded). Further refinement converged to the final values listed in Table I. Table II lists the final atomic coordinates, and Table III contains selected bond distances and angles.

Crystals of $Cp'NbCl_2(ArCCAr)$ (Ar = *p*-tolyl, **3c**) were grown under an inert atmosphere from a toluene solution layered with hexane. The crystal was mounted, and data were collected as described above (Table I). The SHELX set of programs was used to solve and refine the structure. The metal atoms were located with the direct methods program, and subsequent difference maps revealed the location of all non-hydrogen atoms. After convergence with anisotopic temperature factors, H atoms were introduced at calculated positions ($d$(CH) = 1.10 Å; $U_H$ = 0.05), and subsequent refinements yielded the values listed in Tables I, IV, , and V.

## Results and Discussion

**Synthesis.** Reduction of $CpMCl_4$ (M = Nb, Ta) with excess Al powder under an atmosphere of CO gives good (Ta) to excellent (Nb) yields of $[CpMCl(CO)_2]_2(\mu\text{-}Cl)_2$ according to eq 1. The structure of **1a** was confirmed by a single-crystal X-ray analysis.



(1)

**1**: R = H; M = Nb
**1a**: R = Me; M = Nb
**2**: R = H; M = Ta

These complexes are soluble in donor solvents, e.g. THF and acetonitrile, but sparingly soluble or insoluble in other common organic solvents. Spectroscopic evidence suggests that the chloro bridges are displaced by donor solvents according to eq 2. In nondonor solvents, e.g. toluene, **1** and **2** display singlets in the $^1H$ NMR spectra corresponding to the equivalent Cp groups. In acetonitrile, two peaks of different intensities were observed corresponding to the equilibrium concentrations of dimer and solvated monomer.

$$[CpMCl(CO)_2](\mu\text{-}Cl)_2 + L \rightleftarrows 2CpMCl_2(CO)_2L \quad (2)$$

It was originally reported that the reaction of $CpMCl_4$ and Al/CO gives the 18e tricarbonyl monomer $CpM(CO)_3Cl_2$.[8] Since interconversions, e.g. $Mn_2(\mu\text{-}Cl)_2(CO)_8 + 2\,CO \rightleftarrows 2ClMn(CO)_5$,[19] are well-known, it seemed possible that during handling, an initially formed tricarbonyl complex lost CO to form the dimeric compounds **1** and **2**. We have shown elsewhere, however, that **1** does not react with CO at room temperature. In fact, in refluxing THF CO is lost and the resulting intermediate forms paramagnetic, mixed-valence $Nb_3$ clusters.[11] Apparently, $CpNbCl_2(CO)_3$ is unstable because the $d^2$ configuration of Nb(III) cannot support three $\pi$-acid carbonyl ligands. Carbonyl complexes generally have a ratio of d electrons to carbonyl groups ≥1 and never as low as $^2/_3$.

The $\nu_{CO}$ bands reported for "$CpTaCl_y(CO)_x$" by Herrmann et al.[9] do not agree well with those we find for **2**. Schrock and co-workers have also reported[20] a compound

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(18) *International Tables for X-Ray Crystallography*; Ibers, J. A.; Hamilton, W. C., Eds.; Kynoch Press, Birmingham, England, 1974; Vol. IV, Tables 2.2 and 2.3.1.

(19) (a) Abel, E. W.; Wilkinson, G. *J. Chem. Soc.* **1959**, 1501. (b) Bamford, C. H. *J. Chem. Soc., Dalton Trans.* **1972**, 1846.

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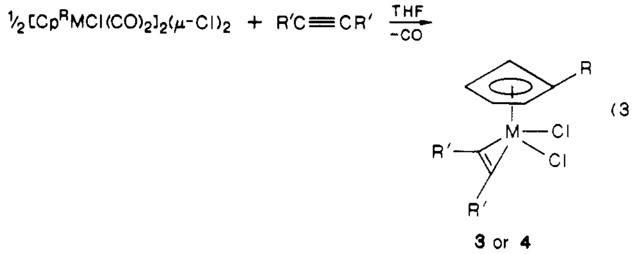
formulated as $CpTaCl_2(CO)_2$ that is probably identical with **2**, but the reported IR spectrum does not agree well with either **2** or Herrmann's material. Arnold and Tilly[21] found $Cp^*TaCl_2(CO)_2$ (THF) as one of the products from the reaction of $Cp^*TaCl_3(SiMe_3)$ with CO in THF. Here, the bulky Cp* (= $C_5Me_5$) ligand may inhibit dimerization, and the presence of THF supports our suggestion (see above) that **1** and **2** are in equilibrium with solvated monomers in donor solvents.

It was of interest to see if the reduction of $CpMCl_4$ in the presence of other ligands would provide efficient syntheses of other Nb(III) and Ta(III) complexes. In particular, direct routes to alkyne complexes of these elements were desirable. The reaction of **1a** with Al in the presence of di-*p*-tolylacetylene gave a 70% yield of the alkyne adduct $Cp'NbCl_2(ArCCAr)$ (**3c**). However, this direct route failed to give Ta(III) alkyne complexes.

A more convenient route to Nb(III) or Ta(III) alkyne complexes was found to be simple CO substitution on **1** or **2** according to eq 3. Yields are 90–95%, and the method is considerably more convenient than one reported previously.[22]



**3** or **4**

**3a**, R = H, R′ = Ar, M = Nb; **b**, R = H, R′ = Ph, M = Nb; **c**, R = Me, R′ = Ar, M = Nb; **d**, R = Me, R′ = Ph, M = Nb; **e**, R = H, R′ = Et, M = Nb; **4a**, R = H, R′ = Ar, M = Ta; **b**, R = H, R′ = Ph, M = Ta; Ar = *p*-toly

The reactions depicted in eq 3 proceed smoothly in THF at room temperature accompanied by CO evolution and a color change from cherry red to a deep, dark red. In toluene at room temperature, no reaction was observed unless a few drops of THF were added. Presumably, the THF cleaves the dimer (cf. eq 2) to produce the solvated monomer which reacts with the alkyne. The reaction is faster with the Nb complexes. Varying the alkyne/metal ratio from 2:1 to 1:2 produced only the monoalkyne adducts, **3** or **4**, and no evidence (IR) for any intermediate species was seen.

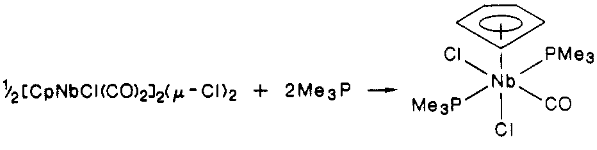
Species **3** and **4** are 16e complexes if the coordinated alkyne is counted as a 4e donor. In fact, the $^{13}C$ NMR chemical shift of the alkyne carbons appear in the range, $\delta$ 215–220, associated with 4e-donor alkyne ligands.[23]

In spite of their *apparent* electronic unsaturation, these complexes show no tendency to add other ligands. In particular, **3** or **4** failed to react with CO (4 atm) or with excess PhCCPh in refluxing toluene (after 48 h the initial alkyne complex was quantitatively recovered and there was no evidence for alkyne exchange).

These observations paralleled those of Schrock et al.[24] who found that $Cp^*TaCl_2(PhC{\equiv}CPh)$ did not react with excess alkyne. This result contrasts sharply with the reactivity of Nb(I) alkyne complexes: $CpNb(CO)_2(PhC{\equiv}CPh)$ reacts with added alkyne to yield $CpNb(CO)(PhC{\equiv}CPh)_2$ which reacts further to give hexaphenylbenzene and $CpNb(CO)(PhC{\equiv}CPh)(\eta^4\text{-}C_4Ph_4)$.[25]

The carbonyl dimer (**1**) reacts with excess phenylacetylene to give triphenylbenzene (primarily the 1,3,5-isomer). Acetylene is polymerized to a mixture of *cis*- and *trans*-polyacetylene by THF solutions of **1** or **1a**. No pure acetylene metal adducts could be isolated, but a paramagnetic complex has been isolated from the reaction of **1** with 1 equiv of PhCCH. This compound is currently under investigation.

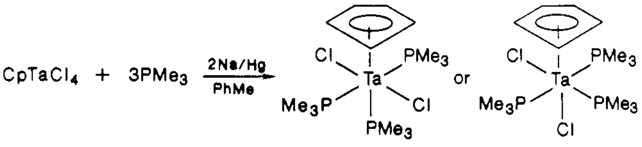
The reactions of **1** with phosphines contrasts with the reactions with alkynes. With phosphines, only one CO is displaced to give 18e compounds of the type $CpM(CO)Cl_2L_2$ (eq 4). The remaining carbonyl in **5** is very resistant to further substitution. Complexes analogous to **5** have been obtained previously.[14]



**5**

(4)

A fully substituted Ta(III) phosphine complex could be obtained by reduction of $CpTaCl_4$ in the presence of ligand (eq 5). $^1H$ NMR establishes that two $PMe_3$ ligands are trans to one another. The remaining phosphine may be either axial or equatorial as shown below.

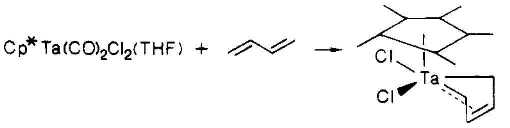


**6a** **6b**

(5)

Previous work on $CpMoP_2Cl_3$ complexes showed that coupling between the Cp protons and phosphorus was observed only when the phosphorus was trans to the Cp group ($J_{PH} \sim 2$ Hz).[26] In complex **6**, however, the Cp resonance was split into an ill-resolved quartet ($J_{PH}$ = 2.8–3.2Hz) from nearly equivalent coupling to all three phosphorus nuclei. Hence, isomer **6b** is favored because all three P atoms are similarly placed with respect to the Cp group, but the question of why the coupling to the equatorial phosophines is large compared to the $CpMoP_2X_3$ complexes remains open.

Several attempts were made to displace carbonyl ligands of **1** with dienes, e.g. 1,3-cyclohexadiene, isoprene, 2,3-dimethylbutadiene, and butadiene. Reaction was observed only with the unsubstituted butadiene, but the brick-red product was too insoluble to characterize adequately. The product of the reaction of butadiene with $Cp^*Ta(CO)_2Cl_2(THF)$ (eq 6), however, gives a product identical with that reported from the reaction of $Cp^*TaCl_4$ and $(MgC_4H_6)_x$.[15,27]



(6)

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[26] Stärker, K.; Curtis, M. D. *Inorg. Chem.* **1985**, *24*, 3006.

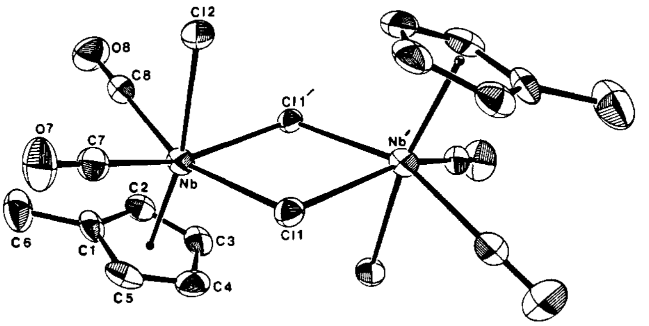


**Figure 1.** ORTEP plot (50% probability thermal ellipsoids) of the molecular structure of $[Cp'NbCl(CO)_2]_2(\mu\text{-}Cl)_2$ with the numbering scheme.

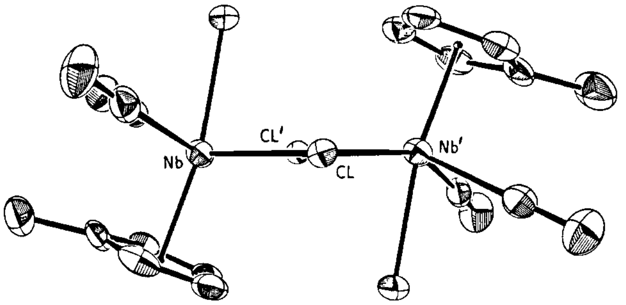
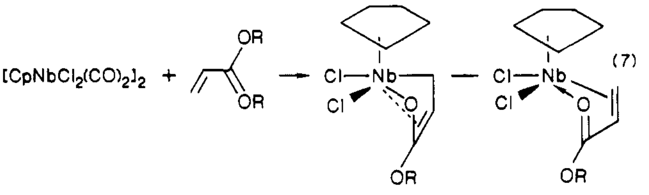


**Figure 2.** ORTEP plot of a side view of the structure of **1a**.

Similarly, acrylate esters displace CO from **1** to give bright yellow adducts (eq 7). Even for R = Bu, the compounds are so sparingly soluble that X-ray quality crystals could not be obtained. Presumably, the structures of **7a**–**7c** are similar to that of the compound obtained from "$CpTaCl_x(CO)_y$" and 2-methyl-2-penten-4-one, $Me_2C{=}CHC(O)Me$.[9] Similar electronic rearrangements are observed for butadiene–metallocyclopentene structures.[27]



**7a–c**, R = Me, Et, Bu

**X-ray Structure Determinations. A. $[CpNbCl(CO)_2]_2(\mu\text{-}Cl)_2$.** Figure 1 presents an ORTEP plot of the molecular structure of **1a**. The molecule resides on a crystallographic inversion center, so the $Nb_2Cl_2$ core is strictly planar. The idealized (noncrystallographic) symmetry is $C_{2h}$. All Nb–Cl(bridge) bonds have identical lengths (2.604 [1] Å) within experimental error. The long Nb⋯Nb distance (4.051 (1) Å) and the obtuse Nb–Cl1–Nb′ angle (101.45 (4)°) indicate a lack of any significant Nb–Nb bonding interaction.

The terminal Nb–Cl bonds (2.495 (1) Å) are considerably shorter than the Nb–Cl bridge bonds. This may reflect increased π bonding in the terminal Nb–Cl bonds or the trans effect of the CO groups on the bridge bonds. The two carbonyl groups are cis to one another (OC–Nb–CO = 88.1 (2)°) and trans to the bridging chlorides. The carbonyls do not lie in the $Nb_2Cl_2$ plane (Figure 2), and the Cp–Nb–Cl2 axis is also displaced such that the geometry around each Nb atom resembles a four-legged piano stool ($CpNbCl_2(CO)_2$) with an added, axial chloride ligand.

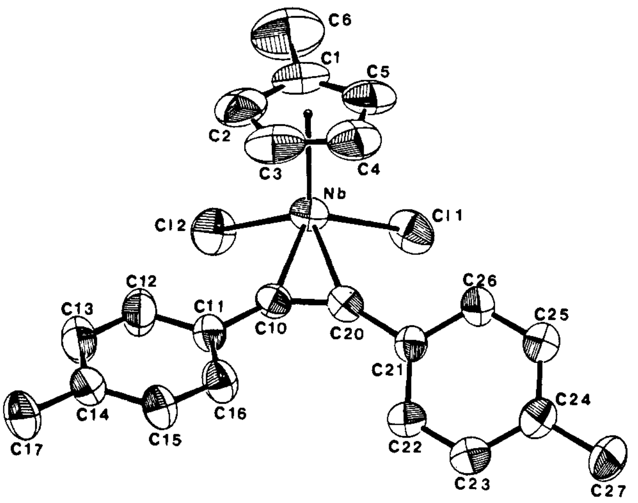
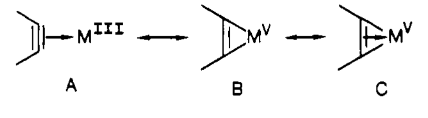


**Figure 3.** ORTEP plot (50% probability thermal ellipsoids) of the molecular structure of Cp′NbCl2(ArCCAr) (Ar = *p*-tolyl, **3c**) with the numbering scheme.

Compounds **5** and **6** are believed to have the same geometry about the metal as does $CpTaCl_2(CO)(PMe_2Ph)_2$.[14] As in the latter compound, the metal–chlorine bonds are 0.1–0.2 Å longer than expected[14] as a result of the trans effect of the CO and Cp ligands.

**$Cp'NbCl_2(ArCCAr)$ (3c, Ar = *p*-Tolyl).** Figure 3 is an ORTEP drawing of the molecular structure of **3c**. If the alkyne ligand is considered to occupy one coordination site, the structure may be described as a three-legged piano stool. The Nb–Cl bond distances (average 2.36 Å) are much shorter than those found in **1a** above. We attribute the shortness of these bonds in **3c** to enhanced Nb–Cl π bond in the formally 16-electron complex.

The most interesting aspect of the structure is found in the bonding between the metal and the coordinated alkyne. The Nb–C10 and Nb–C20 distances are short, 2.07 Å (average). This distance is just outside the range expected for a Nb=C *double* bond (1.98–2.0 Å),[28] and the C—C separation (1.307 (7) Å) corresponds to a bond order of ca. 2.2 (obtained from a plot of bond orders vs C–C distance). The C–C–Ar angle (143°) shows a considerable distortion from the free ligand as was found for the complex $Cp^*Ta(PhCCPh)Cl_2$.[24] The short M–C and long C–C distances, combined with the large C–C–Ar angle, are indicative of strong d→π* back-bonding, and these complexes may be viewed as metallacyclopropenes with the metal in a formal +5 oxidation state:[29–31]



**EHMO Description of the Bonding in $CpM(alkyne)X_2$ Complexes.** Several questions concerning the nature of the bonding of alkyne complexes to early transition metals were raised in the course of this work. One question is related to the nature of the alkyne metal interaction; which of the resonance extremes, A–C above, best represents the bonding? A related question is the following: Why does one alkyne displace two carbonyls

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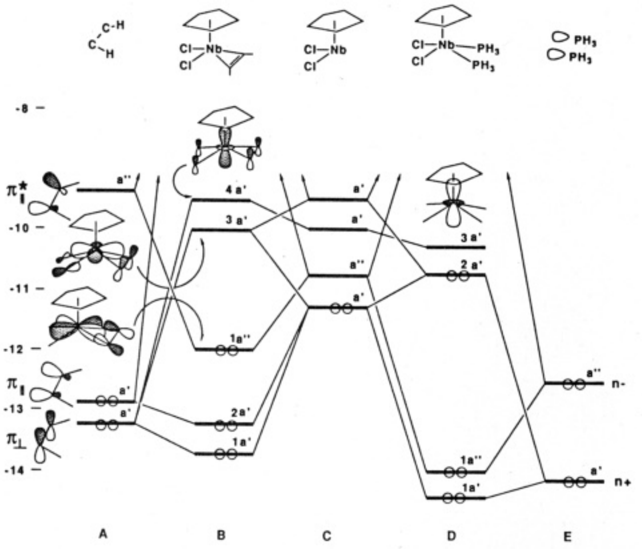

**Figure 4.** EHMO energy level diagrams for the interaction of the $CpNbCl_2$ fragment molecular orbitals (FMO's) with an alkyne or two phosphines: (A) alkyne FMO's; (B) MO energies of $CpNbCl_2(HCCH)$; (c) $CpNbCl_2$ FMO's; (D) MO energies of $CpNbCl_2(PH_3)_2$; (E) $(PH_3)_2$ FMO's.

from **1** to form an apparently unsaturated complex, **3**, whereas phosphines displace only one carbonyl ligands to give 18e complexes, e.g. **5**? These issues have been explored with the aid of EHMO calculations.[32]

The differences in the energy levels of complexes **3** and **5** were ascertained by determining how the $CpNbCl_2$ fragment molecular orbitals (FMO's) interact with the FMO's of (a) a $C_2H_2$ ligand and (b) two $PH_3$ ligands. Bond lengths and angles in the fragments corresponded to those observed experimentally. Parts A, C, and E of Figure 4 show the frontier energy levels of the FMO's of the HCCH, $CpNbCl_2$, and $(PH_3)_2$ fragments, respectively. Parts B and D of Figure 4 depict the energy levels of the complexes $CpNbCl_2(HCCH)$ and $CpNbCl_2(PH_3)_2$, respectively.

In order of increasing energy, the frontier FMO's of $CpNbCl_2$ are essentially the $x^2 - y^2$, $xy$, $z^2$, $yz$, and $xz$ d orbitals. The $xz$ orbital is pushed to high energy by an antisymmetric combination of Cl p orbitals (i.e. M–Cl anti-bonding) and is not shown in Figure 4C. The frontier FMO's of the $(PH_3)_2$ fragment are the symmetric and antisymmetric combinations, $n_+$ and $n_-$, of the lone pairs on the $PH_3$ groups (the former lies at very low energy (−16 eV) and is off scale on the figure). The $n_+$ combination interacts with all the a′ symmetry FMO's of the $CpNbCl_2$ fragment, but the interaction with the $yz$ orbital is strongest and the $yz$ is then pushed to high energy while $n_+$ is depressed to lower energies. The antisymmetric $n_-$ combination finds its symmetry mate in the $xy$ orbital with the result that the bonding/antibonding combinations remove $n_-$ and $xy$ from the frontier region. For a $d^2$ complex, these interactions leave the $x^2 - y^2$ orbital as the HOMO and the $z^2$ orbital as the LUMO. A very small HOMO–LUMO gap (0.6 eV) is computed (Figure 4D). There are two consequences of this small HOMO–LUMO gap: (1) a 16e complex, $CpNbCl_2(PH)_3)_2$, is expected to be paramagnetic (either a triplet ground state or a thermally accessable triplet excited state) and (2) the LUMO is an excellent acceptor orbital for another ligand. This acceptor orbital ($z^2$) is aligned along the Nb–Cp axis so an incoming ligand would give rise to the geometry observed for stable 18e complexes of the type $CpMCl_2L_3$ (see above). It is interesting to note that $Cp^*MCl_2(PR_3)_2$ (M = Ta, V) complexes have been synthesized and these apparently have a triplet ground state in agreement with our calculations.[33]

The situation is quite different for the alkyne complex. The HCCH fragment has two symmetric orbitals ($\pi_\parallel$ and $\pi_\perp$) at low energy and an antisymmetric orbital ($\pi_\parallel{}^*$) which lies just above the d manifold of $CpNbCl_2$. The low-energy orbital $\pi_\perp$ forms bonding and antibonding combinations primarily with $z^2$ and elevates the energy of the latter. $\pi_\parallel$ does the same with the $x^2 - y^2$ orbital. The big difference comes in the interaction of $\pi_\parallel{}^*$ with the $xy$ orbital. $\pi_\parallel{}^*$ lies above the $xy$, so the $\pi_\parallel$–$xy$ bonding combination is depressed and becomes the HOMO for a $d^2$ complex (Figure 4B).

In $CpNbCl_2(HCCH)$, a large (2 eV) HOMO–LUMO gap is computed, there is no low-energy acceptor orbital on the metal, and the alkyne complex is perfectly stable with a 16e count. Stabilization of 16e complexes by removal of an orbital from the bonding/nonbonding region has been noted previously in $\eta^2$–acyl[34] and oxo complexes.[35]

The question of the appropriate description, alkyne complex or metallacyclopropene, was also addressed. The Mulliken overlap population (MOP) of the Nb–C(alkyne) bond is 0.50. This value may be compared to a typical Nb–Me MOP of 0.56 in similar compounds. From the comparison, the NbC(alkyne) bond order approaches unity. The C–C $\pi$-bond order of the alkyne may be obtained from the sum of the number of electron pairs in $\pi_\parallel$ and $\pi_\perp$ minus the number in $\pi_\parallel{}^*$ and $\pi_\perp{}^*$. The computed fragment populations are $\pi_\perp$ (1.68), $\pi_\parallel$ (1.74), $\pi_\parallel{}^*$ (0.81), and $\pi_\perp{}^*$ (0.02). The $\pi$-bond order is thus $(1.68 + 1.74 - 0.81 - 0.02)/2 = 1.3$. Adding the $\sigma$-bond order of 1.0 gives a value of 2.3 for the total C–C bond order. An identical value was obtained from considerations of the MOP's. Note that the computed bond order agrees well with the observed C–C bond distances.

The fragment populations listed above show some interesting features. $\pi_\perp$ donates more electron density to the metal than does $\pi_\parallel$ (0.32 vs 0.26), so the alkyne is regarded as a "4e donor" (see discussion in ref 28a). Rather surprising, however, is the very large degree of back-donation from the metal to $\pi_\parallel{}^*$ (0.81e) which means the alkyne ligand is a *net acceptor* of electrons from the metal. Thus, the metal is formally oxidized, and structure C (above) best represents the metal–alkyne bonding in these complexes.

One further aspect of the alkyne–metal interaction emerged from our calculations. The barrier to rotation of the alkyne was calculated to be ca. 6 kcal/mol. This low value is in agreement with experimental results[24] and with EHMO calculations on similar molecules.[36]

**Conclusions.** Complexes of the type $[CpMCl_2(CO)_2]_2$ (M = Nb, Ta) are easily prepared by reduction of $CpMCl_4$ with Al powder under 1 atm of CO. The carbonyl ligands are readily displaced to give a variety of monocyclopentadienyl complexes of Nb(III) or Ta(III). For the early transition metals, alkynes are shown to be powerful electron acceptors and the alkyne adducts $CpMCl_2(RCCR)$ are

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Table VI

| orbital | | $H_{ii}$, eV | $\zeta_1$ | $\zeta_2$ | $C_1{}^a$ | $C_2{}^a$ |
|---|---|---|---|---|---|---|
| Nb | 5s | −10.10 | 1.89 | | | |
| | 5p | −6.86 | 1.85 | | | |
| | 4d | −12.10 | 4.08 | 1.64 | 0.6401 | 0.5516 |
| Cl | 3s | −26.30 | 2.183 | | | |
| | 3p | −14.20 | 1.733 | | | |
| P | 3s | −18.60 | 1.750 | | | |
| | 3p | −14.00 | 1.300 | | | |

[a] Coefficients in the double-$\zeta$ atomic wavefunction.

best regarded as metallacyclopropenes. Future papers will report the redox and halide substitution chemistry of $[CpMCl_2(CO)_2]_2$.

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## Appendix

In the EHMO calculations, the parameters ($\zeta$ and $H_{ii}$) used for C and H were standard ones contained in the ICON8 program. Those for Nb, Cl, and P are given in Table VI. The bond distances employed were Nb–C(Cp) = 2.34 Å, Nb–C(alkyne) = 2.10 Å, Nb–Cl = 2.36 Å, C–C(Cp) = 1.43 Å, C–C(alkyne) = 1.30 Å, Nb–P = 2.50 Å, P–H = 1.44 Å, and C–H = 1.10 Å. For $CpNbCl_2(HCCH)$, angles were taken from the structure of **1a**, while for $CpNbCl_2(PH_3)_2$, the pertinent angles are Nb–P–H = 116° and CT–Nb–Cl = CT–Nb–P = 110° (CT = centroid of the Cp ring), and the dihedral angle between all CT–Nb–Cl and CT–Nb–P planes was 45°.

**Registry No.** 1, 95765-11-0; **1a**, 95784-23-9; **2**, 95784-24-0; **3a**, 120411-06-5; **3b**, 120411-07-6; **3c**, 95765-12-1; **3d**, 120411-08-7; **3e**, 120411-09-8; **4a**, 103148-33-0; **4b**, 103148-32-9; **5**, 112968-60-2; **6**, 120411-10-1; **7a**, 120411-11-2; **7b**, 120411-12-3; **7c**, 120411-13-4; DPPE, 1663-45-2; $CpNbCl_4$, 33114-15-7; $Cp'NbCl_4$, 62927-89-3; $CpTaCl_4$, 62927-98-4; $CpNbCl_2(CO)DPPE$, 112942-54-8; $Cp^*TaCl_2(CO)_2(THF)$, 98688-40-5; $Cp^*TaCl_2(C_4H_6)$, 95251-00-6; $H_2C{=}CHCH{=}CH_2$, 106-99-0; $H_2C{=}CHCOOMe$, 96-33-3; $H_2C{=}CHCOOEt$, 140-88-5; $H_2C{=}CHCOOBu$, 141-32-2; di-*p*-tolylacetylene, 2789-88-0; diphenylacetylene, 501-65-5; 3-hexyne, 928-49-4; acetylene, 74-86-2; *cis*-polyacetylene, 25768-70-1; *trans*-polyacetylene, 25768-71-2; 1,3,5-triphenylbenzene, 612-71-5; 1,2,4-triphenylbenzene, 1165-53-3; trimethylphosphine, 594-09-2.

**Supplementary Material Available:** Tables VIIS and VIIIS, thermal parameters for **1a** and **3c**, and Tables IXS and XS, bond distances and angles for **1a** and **3c** (4 pages); Tables XIS and XIIS, $F_o$ vs $F_c$ for **1a** and **3c** (15 pages). Ordering information is given on any current masthead page.

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# Mechanism of the Photochemical Cis–Trans Isomerism of $(\eta^5\text{-}C_5Me_5)Re(CO)_2X_2$ (X = Me, Cl, Br, I)

Ross H. Hill* and Bentley J. Palmer

*Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6*

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Photolysis of *cis*-$(\eta^5\text{-}C_5Me_5)Re(CO)_2Me_2$ leads to the isomerism to *trans*-$(\eta^5\text{-}C_5Me_5)Re(CO)_2Me_2$. The mechanism of this reaction has been studied by FTIR spectroscopy at low temperature. It has been determined that photolysis of *cis*-$(\eta^5\text{-}C_5Me_5)Re(CO)_2Me_2$ at 13 K in methylcyclohexane, methylcyclohexene, or (1,2-epoxyethyl)benzene results in extrusion of a carbonyl ligand and the production of $(\eta^5\text{-}C_5Me_5)Re(CO)Me_2$. This molecule undergoes reaction with the photoproduced CO at 100 K to yield only *trans*-$(\eta^5\text{-}C_5Me_5)Re(CO)_2Me_2$. Photolysis of the trans isomer yields the same unsaturated photoproduct. The mechanism of the photochemically induced cis–trans isomerism for the analogous series of dihalides, *cis*-$(\eta^5\text{-}C_5Me_5)Re(CO)_2X_2$ (X = Cl, Br, I) in (1,2-epoxyethyl)benzene, has also been investigated and found to occur by the same sequence of reactions as described above.

## Introduction

We wish to report the results of a study dealing with the mechanism of the photochemical cis–trans isomerism of $(\eta^5\text{-}C_5Me_5)Re(CO)_2X_2$ (X = Me, Cl, Br, I). Our interest in the dimethyl complex was initially to see if the photochemical reaction was CO loss, as expected from various studies of metal carbonyls,[1] or reductive elimination as one may expect from the analogous photoreaction of molecules containing cis one-electron ligands. Reductive elimination has been implicated in the photoreactions of a variety of molecules containing cis one-electron groups, such as $(\eta^5\text{-}C_5Me_5)IrPMe_3H_2$,[2] $(\eta^5\text{-}C_5Me_5)IrPMe_3H(R)$,[2] $(\eta^5\text{-}C_4H_4)Fe(CO)_2H(SiEt_3)$,[3] and $(\eta^5\text{-}C_5H_5)Mn(CO)_2H(SiEt_3)$.[4] It is notable that the latter two undergo reductive elimination of the cis groups rather than CO loss. Photochemical reductive elimination of methyl groups also has some precedent in the literature.[5] Other possible reactions of the metal alkyl groups include radical cleavage[6] and alkyl group transfer to a ring carbon as was observed in the photoreaction of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2R$ (R = Me, benzyl).[7] This last example is interesting in that the photoreaction of the alkyl group occurred in competition with CO loss.

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