

ligand is as compatible as carbonyl or phosphine with catalytic activity. The effect of counterion variation on cyanometallate stability, i.e., **2a** vs. **2c**, is consistent with other observations from this laboratory;¹⁶ the causes of these counterion effects are not well understood, however, and are worthy of further study. Perhaps most importantly, this work emphasizes that organometallic cyanide chemistry in aprotic solvents is possible. This is not a trivial point. There are few previous studies of the reactivity of organocyanometalates in aprotic solvents and, to our knowledge, none in which one low-valent organocyanometalate was converted to another (i.e., 1 → 2).

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Registry No. 1, 88657-44-7; **2a**, 88728-24-9; **3**, 101834-94-0; Ni[P(OCH₃)₃]₄, 14881-35-7; *p*-CH₃C₆H₄CH₂Br, 104-81-4; phenylacetylene, 536-74-3; 1,2,4-triphenylbenzene, 1165-53-3; diphenylacetylene, 501-65-5; 3-hexyne, 928-49-4; 1-butyne, 107-00-6; trimethyl phosphite, 121-45-9; 1,2-di-*p*-tolylethane, 538-39-6.

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Novel Cationic Dinuclear Ruthenium(I) Complexes Containing Carbonyl and Isocyanide Ligands. The X-ray Crystal Structures of [Ru₂(CO)₂(CN-*t*-Bu)₈](PF₆)₂ and [Ru₂(CNCH₂C₆H₅)₁₀](PF₆)₂

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Summary: Nucleophilic substitution reactions on *catena*-[Ru(CO)₂(O₂CCH₃)] with isocyanides provide synthetic routes to the dinuclear ruthenium(I) complexes [Ru₂(CO)₂(CN-*t*-Bu)₈](PF₆)₂, [Ru₂(CO)(CNR)₉](PF₆)₂, and [Ru₂(CNR)₁₀](PF₆)₂ (R = C₆H₅CH₂, 2,6-Me₂C₆H₃) which are derivatives of the unknown d⁷-d⁷ dimer [Ru₂(CO)₁₀]²⁺. The X-ray crystal structures of [Ru₂(CO)₂(CN-*t*-Bu)₈](PF₆)₂ and [Ru₂(CNCH₂C₆H₅)₁₀](PF₆)₂ have been determined.

Homoleptic metal isocyanide complexes and complexes which contain predominantly isocyanide ligands are surprisingly rare when compared to the diversity of metal carbonyl complexes known.¹⁻³ Why this is so is still not clear, but it can probably be related to the different steric and electronic properties of the isocyanide ligand when compared to the carbonyl ligand. We have recently begun

investigating the chemistry of the polymeric ruthenium(I) complexes *catena*-[Ru(CO)₂(O₂CR)]⁴ and of the dinuclear osmium(I) complexes {[Os(CO)₃(O₂CR)]₂}⁴ as precursors to ruthenium(I) and osmium(I) chemistry. Herein we report on the reactions of *catena*-[Ru(CO)₂(O₂CR)] with isocyanides in labilizing alcohol solvents which produce rare examples of dinuclear homoleptic isocyanide complexes and provide the first rational⁵ synthetic route to derivatives of the unknown [M₂(CO)₁₀]²⁺ (M = Fe, Ru, Os) dicationic dimers. Confirmatory X-ray structure determinations on two of these salts have been carried out.

The new dinuclear ruthenium(I) complexes are prepared by treating a suspension of the polymer *catena*-[Ru(CO)₂(O₂CCH₃)] (**1**) in refluxing ethanol with an excess of isocyanide (typically a 6:1 isocyanide:ruthenium molar ratio), followed by precipitation with NH₄PF₆. Short reaction times (<10 min) produce the salts [Ru₂(CO)₂(CN-*t*-Bu)₈](PF₆)₂ (**2**) and [Ru₂(CO)(CNR)₉](PF₆)₂ (**3**, R = C₆H₅CH₂; **4**, R = 2,6-Me₂C₆H₃), whereas more prolonged reaction times (72 h) have been found to yield the homoleptic dimers [Ru₂(CNR)₁₀](PF₆)₂ (**5**, R = C₆H₅CH₂; **6**, R = 2,6-Me₂C₆H₃). Complexes **3** and **4** convert on heating with isocyanide to **5** and **6**, but we have found no evidence, under either thermal or photochemical conditions, for the further substitution of **2** by isocyanide.

Lower substituted dinuclear cations have not been observed in the reactions of **1** with isocyanides in alcohol solvents even with stoichiometric additions of isocyanide. What is observed in these reactions though is the complete consumption of isocyanide with a corresponding partial conversion of **1**. The process by which **1** reacts with isocyanide in alcohol possibly occurs via a combination of routes involving depolymerization of dimeric Ru(I) units by either isocyanide⁶ or solvent molecules^{7,9} giving soluble {[Ru(CO)₂L(O₂CCH₃)]₂} complexes, and the labilization¹⁰ of the acetato ligands in such species to give cationic intermediates of the type [Ru₂(CO)_{*n*}L_{*m*}(O₂CCH₃)]⁺ or [Ru₂(CO)_{*n*}L_{*m*}]²⁺. The effects of the positive charge residing on such intermediates would be expected to favor substitution of carbonyl ligands by the more nucleophilic isocyanide ligands, thus leading to high levels of substitution.

Complexes **2-6** exhibit in solution an unusual spectrum of stereochemical flexibility. For **4** and **6** single methyl

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(5) We have recently also obtained the cation [Ru₂(CNC₆H₅Me-2,6)₁₀]²⁺ as a byproduct of melting [(η⁷,η²-C₆H₁₃)Ru(CNC₆H₅Me-2,6)₄]-PF₆. The X-ray crystal structure of [Ru₂(CNC₆H₅Me-2,6)₁₀](BPh₄)₂ has been determined showing this molecule to possess an eclipsed configuration of isocyanide ligands and a ruthenium-ruthenium bond of 3.003 Å: Chalmers, A. A.; Liles, D. C.; Meintjies, E.; Oosthuizen, H. E.; Pretorius, J.; Singleton, E. *J. Chem. Soc., Chem. Commun.* 1985, 1340.

(6) Neutral complexes of the type [Ru(CO)₂L(O₂CCH₃)₂] (L = donor ligand) can be obtained directly from **1** by reaction in solvents such as benzene or diethyl ether. Lewis and co-workers⁴ have obtained an extensive series of phosphine-substituted products in this way.

(7) The polymer **1** is soluble in donor solvents such as acetonitrile and dimethyl sulfoxide from which the labile complexes [Ru(CO)₂(solvent)(O₂CCH₃)₂]₂^{4,8} can be isolated. In ethanol this solvolysis reaction does not occur as readily, but warming of **1** in ethanol does produce a slight yellow coloration, suggesting the formation of similar species.

(8) Albers, M. O.; Singleton, E., unpublished observations.

(9) Complexes of the type [Ru(CO)₂(solvent)(O₂CCH₃)₂] have been found⁸ to react readily with ligands L to give as products [Ru(CO)₂L(O₂CCH₃)₂]. Indeed, addition of *t*-BuNC to the pale yellow solution obtained by heating **1** in ethanol⁷ gives [Ru(CO)₂(CN-*t*-Bu)(O₂CCH₃)₂]₂, providing evidence for the formation of solvolyzed dinuclear Ru(I) species in ethanol.

(10) We have found that alcohol solvents are particularly effective at promoting cation formation. When reactions are carried out in solvents such as toluene, heptane, or tetrahydrofuran, a range of neutral substitution products are obtained. These will, however, be discussed in more detail elsewhere.

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resonances at 303 K are observed, indicating a dynamic exchange process which equilibrates the axial and the equatorial ligands. The slow-exchange limit is reached for 6 at 283 K when the isocyanide methyl resonances are observed at 2.22 and 2.03 ppm in the expected 1:4 ratio. Thus 4 and 6 provide rare examples of stereochemical nonrigidity in dinuclear complexes containing six-coordinate metal atoms and monodentate ligands.¹¹ Complex 5 is, on the other hand, stereochemically rigid at room temperature as regards the exchange of axial and equatorial ligands, and the expected 1:4 ratio of both methylene and arene signals is observed at 303 K. The high-field (500-MHz) ¹H NMR spectrum of 2 contains five methyl resonances in the range 1.61–1.69 ppm. On cooling, the number of signals increases until at the limit of the temperature range (193 K), 14 major resonances are observed. The narrow range (0.2 ppm) in which these resonances appear has prevented an interpretation of these changes except to conclude that the dimeric structure is probably retained in solution because of the absence of any temperature-dependent chemical shifts or line width broadening. We can only speculate that the large number of methyl resonances at low temperature represents a number of isomers in dynamic equilibrium together with the possibility of nonequivalent methyl groups on individual equatorial isocyanide ligands arising from restricted rotation in the molecule (vide infra).

In order to evaluate factors such as restrictions in the rotation of *tert*-butyl groups and the steric constraints to higher substitution, the X-ray crystal structure of 2 has been determined.¹² Further, as part of a study⁵ to define cone angle limits to homoleptic dimer formation the structure of 5 has also been determined.¹²

The dimeric cations of 2 (Figure 1) and 5 (Figure 2) both lie across a crystallographic twofold axis with the two halves of each molecule linked only by a ruthenium–ruthenium bond (2, 2.886 (2) Å; 5, 2.904 (1) Å). The carbonyl ligands in 2 are located in the equatorial plane of each ruthenium atom and lie in an anti configuration about the ruthenium–ruthenium bond. The equatorial ligands in both halves of the cations of 2 and 5 adopt a staggered conformation with C–Ru–Ru–C dihedral angles in the range 42.4 (6)–50.5 (6)° for 2 and 38.2 (5)–49.9 (5)° for 5. This staggered arrangement is probably a gross reflection

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(12) Crystal data for 2: C₄₂H₇₂F₁₂N₈O₂P₂Ru₂, *M*_r = 1181.16. The crystals are monoclinic, space group C2/c, with *a* = 25.226 (5) Å, *b* = 13.164 (3) Å, *c* = 19.142 (4) Å, β = 93.88 (2)°, *U* = 6342.0 Å³, and *D*_{calcd} = 1.237 Mg m⁻³ for *Z* = 4. Cell parameters and intensity data were measured on a Philips PW1100 four-circle diffractometer with graphite-crystal-monochromatized Mo Kα radiation (λ = 0.710 69 Å) using a crystal of dimensions 0.30 × 0.15 × 0.15 mm. Crystal data for 5: C₈₀H₇₀N₁₀P₂F₁₂Ru₂, *M*_r = 1663.57. The crystals are monoclinic, space group C2/c, with *a* = 27.731 (9) Å, *b* = 15.674 (3) Å, *c* = 19.206 (5) Å, β = 111.33 (3)°, *U* = 7776.16 Å³, and *D*_{calcd} = 1.42 Mg m⁻³ for *Z* = 4. Cell parameters and intensity data were measured on an Enraf-Nonius CAD4F diffractometer with graphite-crystal-monochromatized Mo Kα radiation using a crystal of dimensions 0.48 × 0.22 × 0.15 mm. Data were corrected for absorption and crystal decay. The structures were solved by Patterson and difference electron density synthesis methods and were refined by using Shelx¹³ to current *R* factors of 0.0777 for 307 parameters and 2895 reflections with *F*_o ≥ 4σ(*F*_o) for 2 and 0.0681 for 448 parameters and 3422 reflections with *F*_o ≥ 4σ(*F*_o) for 5. The relatively high *R* factors and a number of abnormally high carbon and fluorine atom temperature factors indicate a considerable degree of disorder within the *t*-Bu and PF₆ groups in 2 and the phenyl and PF₆ groups in 5. Refinements in space groups with reduced symmetry requirements, for example, Cc or C2 (with two independent half molecules in the asymmetric unit) yielded no significant improvements in either the *R* factors or the high-temperature factors for either structure and produced geometries for the two complexes which were essentially similar to those obtained from the C2/c refinements. Models for the disorder are under investigation.

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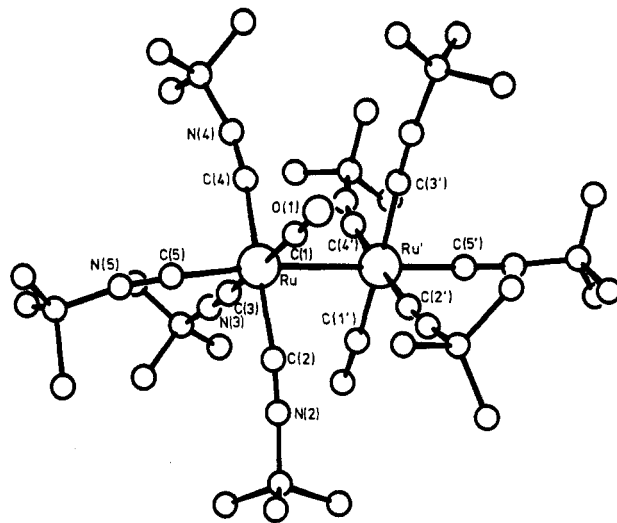


Figure 1. A perspective view of the dimeric cation of 2 showing the atom numbering scheme. Selected bond lengths (Å) and angles (deg): Ru–Ru' = 2.886 (2), Ru–C(1) = 1.89 (2), Ru–C(2) = 2.03 (1), Ru–C(3) = 1.99 (1), Ru–C(4) = 1.99 (1), Ru–C(5) = 2.00 (1), C(1)–O(1) = 1.15 (2), C(2)–N(2) = 1.13 (2), C(3)–N(3) = 1.16 (2), C(4)–N(4) = 1.13 (2), C(5)–N(5) = 1.15 (2), Ru'–Ru–C(1) = 85.1 (3), Ru'–Ru–C(2) = 86.0 (3), Ru'–Ru–C(3) = 90.5 (3), Ru'–Ru–C(4) = 92.4 (3), Ru'–Ru–C(5) = 174.1 (3).

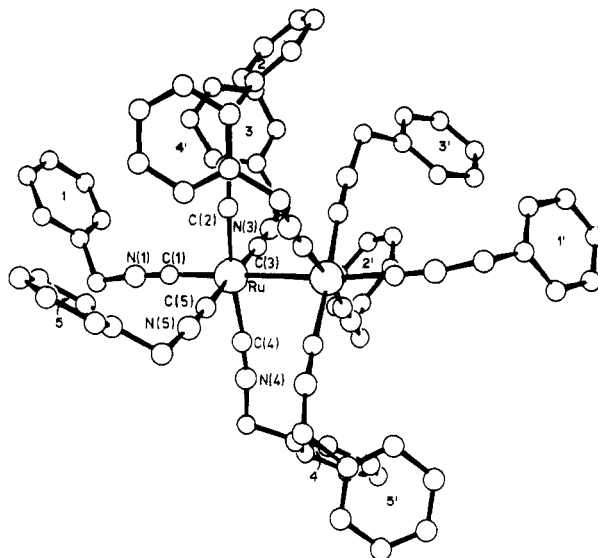


Figure 2. A perspective view of the dimeric cation of 6 showing the atom numbering scheme. Selected bond lengths (Å) and angles (deg): Ru–Ru' = 2.904 (1), Ru–C(1) = 1.968 (9), Ru–C(2) = 1.99 (1), Ru–C(3) = 1.99 (1), Ru–C(4) = 1.99 (1), Ru–C(5) = 1.98 (1), C(1)–N(1) = 1.16 (1), C(2)–N(2) = 1.14 (2), C(3)–N(3) = 1.14 (2), C(4)–N(4) = 1.13 (2), C(5)–N(5) = 1.17 (1), Ru'–Ru–C(1) = 176.6 (2), Ru'–Ru–C(2) = 85.0 (2), Ru'–Ru–C(3) = 88.2 (2), Ru'–Ru–C(4) = 87.9 (2), Ru'–Ru–C(5) = 88.7 (2).

of minimized steric interactions between ligands on opposite metal atoms and in this regard must be considered to be similar to that observed for the isoelectronic dimers [M₂(CO)_{10-n}(CNR)_n] (M = Mn, Re; *n* = 0–4),^{14–16} [Co₂(CNMe)₁₀]⁴⁺,¹⁷ and [M₂(CO)₁₀]²⁻ (M = Cr, Mo).¹⁸ The equatorial ligands in the latter complexes show an overall

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tendency to bend inward toward the opposite metal atom, an effect shown also by all the equatorial ligands in 5 (Ru'-Ru-C in the range 85.0 (2)-88.7 (2)°, but only by the carbonyl ligands in 2 (Ru'-Ru-C(1) = 85.1 (3)°, and by an equatorial isocyanide ligand cis to each carbonyl group (Ru'-Ru-C(2) = 86.0 (3)°). The other equatorial isocyanide ligands in 2 bend away from the opposite ruthenium atom (Ru'-Ru-C(3) = 90.5 (3) and Ru'-Ru-C(4) = 92.4 (3)°). Another interesting effect is observed for 5 where a pair of trans radial isocyanides have the phenyl groups bending inward toward the center of the dinuclear unit, while the phenyl groups of the other ligand pair are bent away from the center of the molecule. In this regard, it is noteworthy that the smallest dihedral angles 38.2 (5) and 39.2 (5)° each involve ligands on opposite ruthenium atoms for which the phenyl groups bend away from the center of the dimer. It is thus apparent that in both 2 and 5, the ligand arrangement reflects reduced steric interactions not only within each half of the molecules but also between each half of the dimers. An examination of the nonbonded contacts for 2 and also of space-filling models further suggests that the ligand arrangement observed crystallographically for 2 represents sterically the best possible arrangement and that the dinuclear unit should be considered to be sterically saturated. It is thus conceivable that the low-temperature ¹H NMR effects can be attributed to nonequivalent methyl groups in individual *tert*-butyl isocyanide ligands, while the introduction of further *tert*-butyl isocyanide ligands is to be considered unlikely due to prohibitive steric interactions, thus possibly explaining the lack of further substitution of 2.

In conclusion, it is clear that the complex *catena*-[Ru(CO)₂(O₂CCH₃)] under suitable experimental conditions provides a most unusual synthetic precursor in ruthenium(I) chemistry. We are actively pursuing this further.

Registry No. 1, 26317-70-4; 2, 101377-32-6; 3, 101377-27-9; 4, 101377-29-1; 5, 101377-30-4; 6, 101402-18-0; Me₃CNC, 7188-38-7; PhCH₂NC, 10340-91-7; 2,6-Me₂C₆H₃NC, 2769-71-3; Ru, 7440-18-8.

Supplementary Material Available: Tables of bond lengths, bond angles, atomic coordinates, and thermal parameters for 2 and 5 and tables of analytical and spectroscopic data for 2-6 (43 pages). Ordering information is given on any current masthead page.

Electrochemical Generation and Reactivity of Bis(triphenylphosphine)platinum(0): An Electrosynthesis of Platinum-Acetylene Complexes

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Summary: Controlled potential bulk reductive electrolysis of *cis*-[PtCl₂(PPh₃)₂] results in the generation of [Pt(PPh₃)₂] in solution. This 2-coordinate, 14-electron compound is efficiently trapped by acetylenes, RC≡CR (R = Ph, COOMe), to produce [Pt(PPh₃)₂(RC≡CR)] quantitatively and by oxidative addition addenda (e.g., C₆H₅COCl, MeI) to produce the corresponding oxidative addition products in high yield. No products arising through ligand disproportionation, Pt(0)/Pt(II) electron transfer, or ligand P-C bond cleavage are produced.

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Stable, 2-coordinate, 14-electron bis(tertiary phosphine)platinum(0) complexes [PtL₂] are well-known where L is sterically demanding, e.g., P(*t*-Bu)₃,¹ P(*t*-Bu)₂Me,² P(*t*-Bu)₂Ph,¹ P(*c*-Hx)₃,^{1,3} or P(*i*-Pr)₃,¹ with chemical reactivity appearing to increase with decreasing steric demand. The unhindered complex [Pt(PEt₃)₂] has been generated photochemically *in situ* from the oxalate [Pt(C₂O₄)(PEt₃)₂] and shown to be extremely reactive toward coordinating and oxidative addition addenda.^{4,5} It is reported⁶ that platinum(0) complexes can be similarly generated from [Pt(C₂O₄)(PPh₃)₂], but the characterization of several of the reaction products has been questioned.⁷ The generation of [Pt(PPh₃)₂] is problematic because of the tendency for ligand P-C bond cleavage to occur in coordinatively unsaturated complexes containing arylphosphine ligands.⁸ Thus, passing nitrogen through solutions of [Pt(C₂H₄)(PPh₃)₂] results in not only loss of ethylene but also formation of benzene and generation of the ortho-metalated phosphido-bridged cluster [Pt₂(μ-PPh₃)₂(PPh₂C₆H₄)₂].⁹ Similarly, thermolysis¹⁰ of [Pt(PPh₃)₄] produces [Pt₂(μ-PPh₂)₂(PPh₃)₂] and [Pt₃(μ-PPh₂)₃(PPh₃)₂Ph] whereas photolysis¹¹ of [Pt(C₂O₄)(PPh₃)₂] under hydrogen does not produce [PtH₂(PPh₃)₂] (cf. the PEt₃ analogue)^{4,5} but rather, after precipitation with NaBF₄, the cluster [Pt₃(μ-PPh₂)₂(μ-H)(PPh₃)₃].[†]

Use of electrochemical methods to generate low-valent intermediates, such as [Pt(PPh₃)₂], has received scant attention in the past, although such methods may show distinct advantages over thermal and photochemical techniques. In the past it has been reported that controlled potential bulk reductive electrolysis of [PtCl₂(PPh₃)₂], followed by addition of HCl gas,¹² yields a hydrido complex, although no details of characterization were given. Interestingly, electrochemical reduction of [PtCl₂(PPh₃)₂], followed by the addition of water, also yields a hydride,¹³ characterized by an IR absorption at 2232 cm⁻¹, whereas electrochemical reduction in the presence of excess triphenylphosphine is reported¹³ to produce [Pt(PPh₃)₃], characterized by elemental analysis only.

Here we report on the controlled potential bulk reductive electrolysis of *cis*-[PtCl₂(PPh₃)₂]¹⁴ to generate [Pt(PPh₃)₂] and trapping reactions with coordinating and oxidative addition addenda. This method provides a versatile synthesis of a diverse range of platinum(0) and platinum(II) complexes from a common precursor. The electrosynthesis is described in detail for the preparation of [Pt(PPh₃)₂(RC≡CR)] complexes on a ca. 50-mg scale.¹⁵

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