

Charge Density in Transition Metal Clusters: Supported vs Unsupported Metal–Metal Interactions

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Experimental X-ray determination of the accurate electron density (ED) in compounds containing transition metals has grown as a major area in the past few years. Most of the progress is due to the recent availability of fast instrumentation like area-detectors (imaging plates¹ or CCD cameras²) which provide full and very accurate datasets in short times also for large unit-cell crystals. The high sensitivity of CCD chips improves the overall quality of the measures, and the large redundancy of data collected allows a more accurate absorption correction, which further favors the study of polynuclear compounds even if they have low *suitability* factors.³ Until now, many experimental studies have been carried on metal dimers, and two recent works have examined the topological features of M–M bonds in unsupported bimetallic compounds.^{2a,4} Few studies of trinuclear compounds are known in the literature,⁵ but these were undertaken when the quantum theory of atoms in molecules (QTAM)⁶ was not yet a common practice among experimentalists.

Here, we report the results of QTAM analysis on the experimental ED of a low nuclearity transition metal cluster. When this work was conceived, for the sake of simplicity “binary” metal–carbonyl clusters were scrutinized, but several difficulties were encountered. Finally, a Co₄(CO)₁₂ derivative of pseudo C_s symmetry, namely, Co₄(CO)₈(μ₂-CO)₃PPh₃ (**1**) (Figure 1), was chosen on the basis of the good quality of the crystals and the neutrality of the species.⁷

The most interesting features to investigate are the differences between the three unsupported and the three carbonyl-bridged Co–Co bonds. According to conventional electron counting rules, both Co₄(CO)₁₂ (**2a**) and Co₄(CO)₉(μ₂-CO)₃ (**2b**) contain six metal–metal bonds; however, differences might arise in the QTAM view. In fact, while each unsupported Co–Co interaction is associated with a bond path (*bp*) and a bond critical point (*bcp*), each Co(μ₂-C_b)Co moiety possesses only the Co–C_b *bps* and *bcps* (Figure 1). All remaining Co–C and Co–P interactions have their *bps* and *bcps*⁸ as well as all intraligand bonds (Table 1); in addition, seven ring critical points (*rcp*, one for each face of the tetrahedron⁹ and one for each phenyl group) and one cage critical

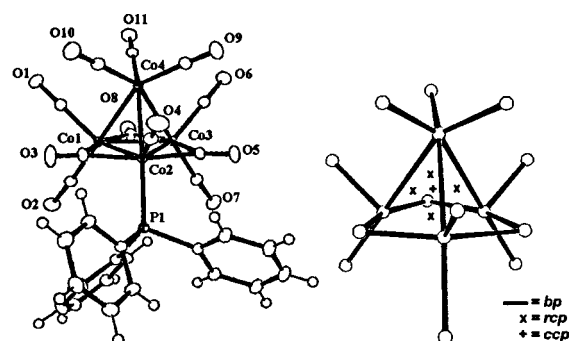


Figure 1. Left: ORTEP view of Co₄(CO)₁₁PPh₃ (ellipsoids for non-hydrogen atoms are drawn at 50% probability); labels of C and H are omitted. Right: Scheme of the principal bond paths and *cps* found for **1**.

Table 1. Averaged Results of the Topological Analysis on **1**

| | <i>d</i> (Å) | $\rho(\mathbf{r}_{bcp})$ (eÅ ⁻³) | $\nabla^2\rho(\mathbf{r}_{bcp})$ (hartree Å ⁻⁵) | $H(\mathbf{r}_{bcp})$ (hartree Å ⁻³) | $G(\mathbf{r}_{bcp})^a$ (hartree Å ⁻³) |
|-------------------------------------|------------------------|---|--|---|---|
| C–H | 1.08(3) | 1.91(8) | –16.4(1.5) | –2.0(1) | 0.84(5) |
| C–C | 1.397(4) | 2.11(3) | –17.1(1.3) | –2.32(1) | 1.12(1) |
| P–C | 1.829(3) | 1.08(2) | –5.5(4) | –1.040(2) | 0.658(1) |
| Co ₂ –P | 2.2418(3) ^b | 0.505[5] ^b | 2.52[1] ^b | –0.199 | 0.375 |
| O _t –C _t | 1.142(3) | 3.34(9) | –4.6(11.3) ^c | –6.1(2) | 5.8(2) |
| O _b –C _b | 1.167(2) | 3.14(4) | –23.2(6.4) ^c | –5.9(4) | 4.3(2) |
| Co _{bas} –Co ₄ | 2.528(8) | 0.252(3) | 1.81(6) | –0.039(1) | 0.166(1) |
| Co–C _t | 1.80(2) | 1.00(3) | 11.5(6) | –0.540(1) | 1.344(5) |
| Co _{1,3} –C _{3,5} | 1.974(3) | 0.67(4) | 6.3(1) | –0.27(4) | 0.71(4) |
| Co ₂ –C _{3,5} | 1.91(1) | 0.73(1) | 8.1(1) | –0.29(1) | 0.858(7) |
| Co _{1,3} –C ₈ | 1.94(1) | 0.76(1) | 7.7(3) | –0.328(8) | 0.865(3) |

^a $G(\mathbf{r}_{bcp})$ is calculated according to Abramov, Y. A. *Acta Crystallogr.* **1997**, A53, 264; for C–C and C–H Bonds, $G(\mathbf{r}_{rcp})$ was estimated adopting the partitioning of sp² carbons. Standard deviations from the mean are reported in parenthesis. C_t, O_t = terminal C, O; C_b, O_b = bridging C, O; Co_{bas} = Co1, Co2, Co3. ^b Standard uncertainty. ^c The large spread of this value (here accounted by the huge deviation from the mean) is due to the C–O *bcp* lying very close to the nodal surface of the Laplacian.^{2a,b}

point (*ccp*, inside the tetrahedron) are found as required by the Poincaré–Hopf rule.¹⁰

Given the observed behavior, a question which might arise as to whether the absence of M–M bond path in the basal plane is due to some bias, possibly related to the short distance between the “missing” M–M *bcp* and the bridging atom, or it is inherent

(7) Homonuclear clusters (like Co₄(CO)₁₂) have disordered structures; other species (like [FeCo₃(CO)₁₂][–]) always presented disorder of the metal cage or reduced scattering despite several trials with different cations. **1** was synthesized as reported by: (a) Cetini, G.; Gambino, O.; Rossetti, R.; Stanghellini, P. L. *Inorg. Chem.* **1968**, 7, 609 and (b) Darensbourg, D. J.; Incorvia, M. J. *Inorg. Chem.* **1980**, 19, 2585. The X-ray structure was originally reported in: (c) Darensbourg, D. J.; Incorvia, M. J. *Inorg. Chem.*, **1981**, 20, 1911. Crystals were obtained by slowly cooling at low temperature a saturated *n*-hexane solution. Crystal data: *a* = 11.748(1) Å, *b* = 16.898(2) Å, *c* = 15.289(1) Å, β = 100.42(3)°, *V* = 2985 Å³, monoclinic, *P*2₁/*n*, *Z* = 4. 155 163 reflections (31 404 independent, $R_{int} = \sum |F_o|^2 - F_{mean}^2 / \sum F_o^2 = 0.0290$) were collected at *T* = 120 K on a SMART CCD area-detector diffractometer, λ = 0.71073 Å (sin θ_{max} / λ = 1.10 Å^{–1}); experimental conditions were similar to those reported in ref 2a. The multipolar model ((d) Hansen, K. H.; Coppens, P. *Acta Crystallogr.* **1978**, A34, 909. (e) Stewart, R. F. *Acta Crystallogr.* **1976**, A32, 565) implemented in software XD ((f) Koritsanszky, T.; Howard, S. T.; Su, Z.; Mallinson, P. R.; Richter, T.; Hansen, N. K. *XD, Computer Program Package for Multipole refinement and Analysis of Electron Densities from Diffraction Data*; Free University of Berlin: Germany, June, 1997) was used to refine the aspherical density, expanding Co and P up to hexadecapoles, C and O up to octupoles, and H up to dipoles. The final agreement indexes were $R1 = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.0190$ and $wR2 = (\sum (F_o^2 - F_c^2)^2 / \sum w F_o^4)^{1/2} = 0.0239$, for the 23523 unique reflections with $I > 2\sigma(I)$.

(8) The terminal CO and the phosphine ligand show good agreement with those of ref 2b.

(9) The basal plane is a six-atom ring (Co₃C₃), while the three lateral faces are four-atom rings (Co₃C).

(10) Collard, K.; Hall, G. G. *Int. J. Quantum Chem.* **1977**, 12, 623.

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(1) Bolotovskiy, R.; Darovsky, R.; Kezerashvili, V.; Coppens, P. J. *Synchrotron Radiat.* **1995**, 2, 181.

(2) (a) Macchi, P.; Proserpio, D. M.; Sironi, A. *J. Am. Chem. Soc.* **1998**, 120, 13429 and references there reported in note 19. (b) Abramov, Y.; Brammer, L.; Klooster, W. T.; Bullock, R. M. *Inorg. Chem.* **1998**, 37, 6317. (c) Scherer, W.; Hieinger, W.; Spiegel, M.; Sirsch, P.; McGrady, G. S.; Downs, A. J.; Haaland, A.; Pedersen, B. *Chem. Commun.* **1998**, 2471.

(3) According to (a) Coppens, P. *Isr. J. Chem.* **1977**, 16, 144 and (b) Feil, D. *ibid.* 149, the ratio $S = V/2n_j|n_j|^2$ (*V* = cell volume, *n_j* = number of core electrons for *j*-th atom) indicates the *suitability* of ED studies (the higher *S* is, the better the system is). Transition metal compounds have small *S* (<0.6), and for **1** *S* = 0.49.

(4) Bianchi, R.; Gervasio, G.; Marabello, D. *Chem. Commun.* **1998**, 1535.

(5) For a review, see: Coppens, P. *Coord. Chem. Rev.* **1985**, 65, 285.

(6) Bader, R. F. W. *Atoms in Molecules: a quantum theory*; International series of monographs on chemistry 22; Clarendon Press: Oxford, 1990.

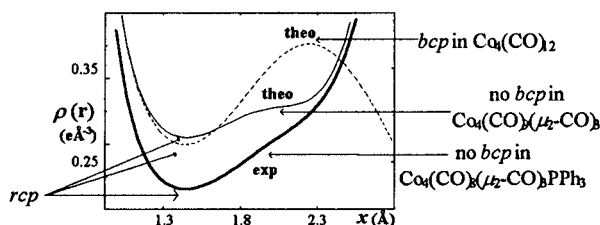


Figure 2. $\rho(\mathbf{r})$ for **1**, **2a**, and **2b** along the line bisecting Co1–Co2–Co3 angle and normal to Co1–Co3 (x is the distance from Co2). The minimum at $x \approx 1.5$ Å corresponds to the *rcp* in the basal plane. The maximum at $x \approx 2.3$ Å for **2a** indicates the presence of Co1–Co3 *bp*, while in the two bridged systems the charge is spread out and the Co–Co *bp* disappears.

to supported interactions. A plot along the line bisecting the Co1–Co2–Co3 angle (and directed perpendicular to Co1–Co3 edge) does clarify the behavior of the electron density (see Figure 2): $\rho(\mathbf{r})$, after the minimum (which corresponds to the *rcp*), rises monotonically toward the carbon and no M–M *bcp* (i.e., a maximum) is found. Ab initio EDs, calculated for **2a** and **2b**,¹¹ allow visualization of what happens in the re-organization of terminal into bridging ligands. Indeed, given the $\rho(\mathbf{r})$ cuts computed along the same direction, it is clear that, upon bridging, the M–M density has been spread out (and not just overwhelmed by the carbon density). Judging from the curvature of the two profiles,¹² charge reorganization is somewhat more “complete” in the experimental than the theoretical model, but the relevant feature here is the difference between the two theoretical shapes.

Thus, according to QTAM, there are no direct metal–metal bonds in the basal plane, and the bridging carbonyls apparently bind at their expense. The current explanation for such behavior stands on the concept of multicenter delocalized bonding;¹³ in fact, each $\text{Co}(\mu_2\text{-C}_b\text{)Co}$ moiety can be seen as a three-center-four-electron bond. This is augmented by the consideration that the stereochemical changes occurring upon transformation from terminal to bridging carbonyls *reorient the directions of maximum bonding* (of the pseudo-octahedral metal fragment): that is, the metal orbital involved in the M–M bond in **2a**, is directed toward C_b in **2b** and **1** (see the Co– C_b *bp* in Figure 3). Having this in mind, we can argue that also in bridged metal dimers, where no *bps* were found,¹⁴ M–M bonding is no longer “direct”, but rather “indirect” because it is obtained through a third part (i.e., the carbonyl).

How can we distinguish a *delocalized* three-center (M–C–M) bond from a couple of *localized* two-center (M–C) interactions? If a comparison with a ketonic carbonyl $\text{RC}(\text{O})\text{R}$ is worthwhile, the $\text{Co}(\mu_2\text{-CO})\text{Co}$ moiety has structural differences such as a shorter C–O distance, a smaller R–C–R angle, and a “shorter” $\text{R}\cdots\text{R}$ contact,¹⁵ all due to an “incomplete” $\text{sp} \rightarrow \text{sp}^2$ rehybridization of the carbon. At the QTAM level one may add that the ketonic carbon has two valence shell charge concentrations

(11) HF/6-311++G** calculation were carried on the hypothetical T_d stereochemistry of **2a** and the experimentally known C_{3v} geometry of **2b** with GAUSSIAN94 package (Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 1995); all Co–Co distances were kept at the values observed for **2b**.

(12) The presence of an almost degenerate critical point (i.e., with rank <3), is related to that of a catastrophe point in the structure space (ref 6, Chapter 3), that is, a structural instability or an easy $C_{3v} \leftrightarrow T_d$ interconversion.

(13) (a) Kostic, M. N.; Fenske, R. F. *Inorg. Chem.* **1983**, *22*, 666. (b) Benard, M. *Inorg. Chem.* **1979**, *18*, 2782. (c) Heijsser, W.; Baerends, E. J.; Ros, P. *Discuss. Faraday Soc. (Symp.)* **1980**, *14*, 211.

(14) (a) Low, A. A.; Kunze, K. L.; MacDougall, P. J.; Hall, M. B. *Inorg. Chem.* **1991**, *30*, 1079. (b) Bo, C.; Sarasa, J. P.; Poblet, J. M. *J. Phys. Chem.* **1993**, *97*, 6362.

(15) Which apparently suggests a comparison with cyclopropanone rather than with a generic keton.

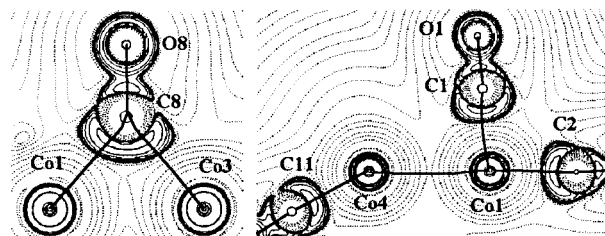
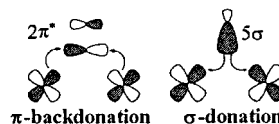


Figure 3. The Laplacian distribution for a bridging carbonyl (left) and the three terminal carbonyl types (right) in **1**; negative contours are solid lines, the superimposed bold lines represent the bond paths. Note the small Co1–C8–Co3 *bp* angle and the large charge concentration on C8. C1, which is bonded in an “equatorial” site, shows a perturbation of $\nabla^2\rho(\mathbf{r})$ toward the apical metal (Co4), a feature which is not observed for “axial” (C2) and “apical” (C11) carbonyls (which lie farther from vicinal metals).

(VSCC),¹⁶ directed toward the R groups, while in $\text{Co}(\mu_2\text{-CO})\text{Co}$ only one, bisecting the Co– C_b –Co angle, is found.¹⁷ This suggests that two separated Co–C *bonded* electrons cannot be localized on each carbon (in agreement, a natural bond orbital analysis on **2b** wave function does not allocate a proper orbital for each Co– C_b bond). The two Co– C_b *bp* lines are quite straight as a result of the presence of both a “central” σ -donation and a lateral π -back-donation, but they are markedly curved at C_b , as a result the Co– C_b –Co *bp* angle¹⁸ is $18(4)^\circ$ smaller than the geometrical one (see Figure 3), in agreement with the hypothesis that donation occurs through the CO 5σ orbital.^{13a}



Some other results of QTAM analysis are worth noting (see Table 1). The density at the Co– C_b *bcp* is more than half the density of Co– C_t bonds, which is an additional proof of the $\rho(\mathbf{r})$ redistribution toward the bridging carbonyls. If compared to $\text{C}_t\text{–O}_t$, $\text{C}_b\text{–O}_b$ has a larger internuclear distance, a reduced bond order (i.e., less density at the *bcp*), and less polarity (the ratio between the kinetic energy density $G(\mathbf{r})$ and $\rho(\mathbf{r})$ at *bcp* is smaller and the carbon basin is larger). The three $\text{Co}_{\text{bas}}\text{–Co}_4$ bonds show features similar to those of M–M bonds in unsupported dimers (at the *bcp*, $\rho(\mathbf{r})$ is small, the Laplacian $\nabla^2\rho(\mathbf{r})$ is positive, the total energy density $H(\mathbf{r})$ is negative, and $G(\mathbf{r})/\rho(\mathbf{r}) < 1$).^{2a}

With this *experimental* work, we have shown that QTAM, at variance from deformation density maps, sheds light on the differences between supported and unsupported M–M interactions, confirming that the M–C–M bond is a delocalized three-center interaction and that M–M bonding is *indirect* because it is achieved through the carbonyl. Moreover, it may be worth noting that $\text{Co}_4(\text{CO})_{11}\text{PPh}_3$ is one of the larger (and less suitable)³ molecules studied until now with this technique; nevertheless, the internal (with respect to the C_v pseudo-symmetry) and external (with respect to theoretical computations) coherence of the derived parameters is qualitatively good, thus suggesting that the experimental limit is still to be reached. For these reasons, we are now planning a study on octahedral clusters containing the $\text{Co}_3(\mu_3\text{-CO})$ moiety, not yet characterized even theoretically.

Supporting Information Available: Tables detailing the experimental and theoretical results (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(16) According to Bader (see ref 6, chapter 7) a VSCC is a maximum of $L(\mathbf{r}) = -\nabla^2\rho(\mathbf{r})$ in the valence region and can be associated to bonded electrons within Lewis formalism.

(17) In **1**, one of the three bridging carbonyls actually shows two (very close) VSCCs toward the metals, while the other two C_b have only one in agreement with the theoretical results on **2b** (see also ref 14b).

(18) Averaged over the three independent bridges; the theoretical value is 27° .